Pratima Bajpai

Green Chemistry and Sustainability in Pulp and Paper Industry

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Preface

Rising raw material prices, increasing waste disposal costs and expanding legislation are the major drivers behind the rise of sustainable technologies. Producers around the world are forced to evaluate their production processes and to search for alternative technologies with lower environmental impact. A comprehensive technology mapping can help producers to compare sustainable technologies and to select viable alternatives.

With increasing regulatory pressure and growing market demand for better products, the pulp and paper industry faces many challenges and must find new ways to improve environmental and process performance and reduce operating costs. There has been a growing demand in the pulp and paper industry to adopt waste minimization strategies in order to create a minimum impact mill. A minimum impact mill does not strictly mean a zero-discharge mill, but rather one which either has no discharge or whose effluent discharge has a minimum or no impact on the environment. The goal of minimum impact mills is to minimize natural resource consumption (wood, water, energy) and minimize the quantity and maximize the quality of releases to air, water and land taking into account economic aspects and working environments. The minimum impact mill makes optimal use of its raw materials; reduces air emissions, water usage, and waste generation; and is a net producer of electricity. The vision of minimum impact manufacturing has captured the imaginations of industry leaders and the environmental community alike. This book gives updated information on minimum impact mill technologies which can meet the environmental challenges of the pulp and paper industry and describes some of the newest twenty first-century fibre lines.

Patiala, India Pratima Bajpai

Contents

Abbreviations

AOX	Adsorbable organic halides
APMP	Alkaline peroxide mechanical pulp
BCTMP	Bleached chemi-thermo-mechanical pulp
BFR	Bleach filtrate recovery
BLS	Black liquor solids
BOD	Biochemical oxygen demand
CBC	Continuous batch cooking
CLB	Closed loop bleaching
COD	Chemical oxygen demand
CTMP	Chem-thermo-mechanical pulp/pulping
DD	Drum displacer
DIP	Deinked pulp
DS	Dry solids
DSC	Dry solids content
DTPA	Diethylene triamine pentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
EGSB	Expanded granular sludge blanket
EPA	Environment protection agency
ESP	Electrostatic precipitator
GHG	Greenhouse gas
HAPs	Hazardous air pollutants
HYP	High-yield pulp
IC	Internal circulation reactor
MBBR	Moving bed biofilm reactor
MCC	Modified continuous cooking
MIM	The minimum-impact mill; minimum-impact manufacturing
NSSC	Neutral sulfite semi-chemical
PCDDS	Polychlorinated dibenzodioxins
PCDFS	Polychlorinated dibenzofurans
P-RC	APMP preconditioning refiner chemical-treatment alkaline peroxide mechanical pulp

RDH	Rapid displacement heating
SS	Suspended solids
TCDD	Tetrachlorodibenzodioxin
TCDF	Tetrachlorodibenzofuran
TEF	Totally effluent-free
TMP	Thermomechanical pulp/pulping
TRI	Toxics release inventory
TRS	Total reduced sulphur
TSS	Total suspended solids
UASB	Upflow anaerobic sludge blanket
VOC	Volatile organic compounds

List of Figures

List of Tables

Chapter 1
General Background

Abstract The pulp and paper industry is one of the most important industries in the world. The global demand for paper products is significant, evidenced by the more than 400 million tons produced annually. In today's world of scarce raw materials, increasing energy costs and talent shortages, managing resources more sustainably is becoming a potential game changer for all sectors. Pulp and paper companies today are highly motivated to operate sustainably and there has been a growing demand to adopt waste minimization strategies in order to create a minimum impact mill which means a concept with a broader range of issues and challenges covering minimisation of resource and emissions, minimising cross-media effects, taking into account economic aspects and working environments. The general background on Green Chemistry and Sustainability in Pulp and Paper Industry is presented.

Keywords Pulp and paper industry • Sustainability • Minimum impact mill • Waste minimization • Emission

The pulp and paper industry is highly diversified in terms of products, raw materials, product qualities, distribution channels, and end uses. RISI (2014) reports that despite the continuous decline in North America and Europe, global paper and board production advanced 0.8 % to reach a new record level of 403 million tonnes in 2013. It has been predicted that global production in the pulp, paper and publishing sector will increase to 500 million tonnes by 2020. Positive growth in tissue and packaging grades continued to offset the retreat in global graphic paper production. China has maintained the top spot for both demand and production of total paper and board over the last 5 years, with the United States remaining in second place. China accounted for 25 % of world demand and 26 % of global production of total paper and board in 2013. In terms of pulp production, the United States remained the top producing country in the world with 49.4 million tonnes in 2013. Canada stood second, producing 17.3 million tonnes, with China a close third at 17.1 million tonnes.

The world's largest paper and paperboard producers are China, United States, Japan, Germany, Canada, Finland, Republic of Korea, Indonesia, Sweden and Brazil, whereas the largest pulp producers are United States, China, Canada, Brazil, Sweden, Finland, Japan, Russian Federation, Indonesia and Chile.

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Inspite of the advancement of digital technology paper consumption is increasing and growth is set to increase as demand in Asia and emerging nations increases. New technology has resulted in a decrease in consumption of newsprint in the United States and Western Europe. But less than half of the wood pulp produced in 2013 was made into printing, writing and newsprint paper. The rest was made into other products including cardboard packaging, toilet tissue and paper towels. Demand for these products is continuously increasing in emerging markets. China has led the increase in demand. China accounted for about 15 % of global paper demand ten years ago. Currently, it accounts for around 25 %, making it the largest consumer of paper in the world ahead of the United States and Western Europe at 18 and 17 % respectively. Worldwide paper use has grown an average 1.7 % each year over the past decade. Inspite of this, China's paper use per person is still only a one third of that in the United States (74 kg against 228 kg). Consumption is expected to increase further as China and other emerging markets continue to grow, with an estimated 650 million people set to join Asia's urban population in the next 20 years. Urbanisation tends to be associated with an increasing demand for hygiene and consumer products containing paper, such as toilet tissue, hand towels and cleaning wipes. Globally paper use has grown an average 1.7 % each year over the past decade. Consumption is expected to grow at an annual rate of 2.4 % over the next 5 years, driven by emerging market demand. Recycled paper accounts for around 55–60 % of global production. However, paper can be recycled only a handful of times before the fibres break down and become unusable. Some countries mandate the use of non-recycled paper in certain types of packaging, for example, when it comes into contact with food. This means that increasing demand for paper also drives up demand for wood pulp, the main raw ingredient for new paper. The United States is the world's largest producer of wood pulp, followed by China and Canada. However, global patterns of production are changing. Improved cultivation techniques have significantly increased the potential yield per hectare of some species of tree. Eucalyptus, originally from Australia, has become popular, and grows well in Latin America – a region that is increasingly important in pulp production. Brazil, for example, has more than doubled pulp production in the last two decades, overtaking countries such as Sweden, Finland and Russia. Eucalyptus can grow all year round in Brazil and reach maturity within 6–7 years. Trees in North America or Scandinavia, where growth stops during winter, can take 25 years to be ready for harvest. Brazil currently produces 40 % of the hardwood pulp sold worldwide. This could increase to 60 % over the next 10 years. Though China is a significant producer of pulp, domestic demand continues to outstrip domestic supply. Around 30 % of Brazil's pulp exports go to China. With China's demand for paper likely to continue to increase, Brazil's pulp exports to China are set to grow in the coming years. Paper is another sector demonstrating the south-south trade flows that are increasingly important to the global economy.

Pulp and paper production, consumption and wasting have several negative environmental and social impacts. The pulp and paper industry is among the world's largest producers of air and water pollutants, waste products, and the gases that cause climate change. It is also one of the largest users of raw materials, including fresh water, energy, and forest fibers. Forests that are essential for clean air and water, wildlife habitat, climate protection, spirituality, recreation and indigenous peoples' cultural survival – including old-growth and other ecologically important forests – are being logged for fiber; in many places they also are being cleared for replacement by plantations that have reduced ecological value and employ toxic chemical herbicides and fertilizers. The pulp and paper industry also has negative effects on the health, well-being and stability of local communities. In North America the majority of paper products are buried in landfills or burned in incinerators which result in significant pollution, forest destruction and major climate change impacts. Industrialized nations, with 20 % of the world's population, consume 87 % of the world's printing and writing papers (Toepfer 2002). Global production in the pulp, paper and publishing sector is expected to increase significantly (OECD 2001). While paper and paper products yield many benefits, due to society's growing demand for paper and the industry's unacceptably large ecological footprint on the planet, it is necessary to transform global paper production and consumption towards processes that are ecologically and socially responsible and sustainable (Environmental Paper Network 2002). The pulp and paper industry has undergone some important changes in environmental performance in the last three decades. According to some observers, this is quite surprising for an industry that has often been taken as an example of a mature sector with a low rate of innovation (Reinstaller 2005).

Inspite of the development of information and communication technology, paper production still remains one of the industrial activities regarded as a pointer to industrialization and educational development worldwide, and, without any doubt, pulp and paper production capacity is increasing (Ogunwusi and Ibrahim 2014). It is one of the high demand sectors in the world of industrial production (Sridach 2010). In the light of this, and also in view of the increasing protectionism of the environment, research and development in the sector have concentrated on overcoming environmental problems associated with pulp and paper manufacturing activities globally. For example pulp and paper production is regarded as the fourth highest consumer of energy globally (Gielen and Tam 2006). It is also a major cause of deforestation, effluent discharge, air and water pollution (Anslem and Oluighbo 2012).

There is no single definition for sustainability, perhaps because it is a process or journey, rather than a state or endpoint. In the academic literature there are hundreds of definitions (Lélé 1991; Low and Gleeson 2005; Marcuse 1998; Mawhinney 2002). Therefore the term 'sustainable' or 'sustainability' is difficult to define and context dependant. A preferred definition of environmental sustainability is "the ability to maintain things or qualities that are valued in the physical environment" (physical environment includes the natural and biological environments) (Sutton 2004). A commonly referenced definition is from the Brundtland Report (UN General Assembly 1987) which defines sustainable development as "…development that meets the needs of the present without compromising the ability of future generations to meet their own needs". The United States Department of Commerce defines sustainable manufacturing as "the creation of manufactured products that use processes that minimize negative environmental impacts, conserve energy and natural resources, are safe for employees, communities, and consumers and are economically sound." Another organization defines sustainable manufacturers as those who "use world-class manufacturing and environmentally friendly practices to improve the profitability of their business and reduce their impact on the environment." The Organisation for Economic Co-operation and Development (OECD) defines the general principle of sustainable manufacturing "to reduce the intensity of materials use, energy consumption, emissions, and the creation of unwanted by-products while maintaining, or improving, the value of products to society and to organizations." The OECD also relates the term 'sustainable manufacturing' to 'eco-innovation'. The latter is described as the trigger to developing a green economy and thus assisting manufacturing to become, sustainable (Sustainable Manufacturing Initiative 2011).

A sustainability issue arises whenever a valued system, object, process or attribute is under threat. The existence of the valued system, object, process or attribute could be threatened or its quality could be threatened with serious decline. In other words there is a sustainability issue whenever there is something that is valued that faces the risk of not being maintained. Whenever there is a strong sense of urgency, there is always a sustainability issue involved. This urgency could relate to something that already exists or to an understood potential.

Pulp and paper companies have faced environmental issues for many years because of the resource-intensive nature of their industry contributing to several environmental problems which include global warming, human toxicity, ecotoxicity, photochemical oxidation, acidification, nutrification, and solid wastes (Blazejczak and Edler 2000). Most noticeable have been allegations from NGOs against companies running logging activities in primary forest to supply fiber for their chemical or mechanical pulping operations. These allegations and the complaints from other civil society groups against the industry, have led governments to strengthen environmental regulations, initially in the developed world, but currently the regulatory trend is global. Frequently changing regulations have thus shaped the pulp and paper industry for decades and are continuing to shape it globally. This has resulted in many innovations – a new form of raw material, recycled fiber, to name just one. For obvious commercial reasons, Pulp and paper companies today are also, intrinsically highly motivated to operate sustainably, for example, to ensure a sufficient flow of fiber into their mills from nearby forests or plantations.

In today's world of scarce raw materials, increasing energy costs and talent shortages, managing resources more sustainably will become a potential game changer for all sectors. This is particularly true for resource intensive sectors like the forest product industry. If pulp and paper companies address this new reality proactively, they will both avoid unnecessary costs and capture opportunities to create significant value. The key to success is to embed sustainability – environmental, operational and even social sustainability- as an objective into every management decision, at every level of the organization. Table 1.1 shows goals in pursuit of an environmentally and socially sustainable paper production and consumption system.

Table 1.1 Goals in pursuit of an environmentally and socially sustainable paper production and consumption system

Minimize paper consumption
Eliminate excessive and unnecessary paper consumption
Clean production
Minimize the combined impacts of water, energy, wood, and chemical usage, air, water, solid waste, and thermal pollution across the entire paper production system including: fiber production/sourcing, pulping, production, transportation, use, and disposal.
Eliminate harmful pulp and paper mill discharges and the use of chlorine and chlorine compounds for bleaching.
Responsible fiber sourcing
End the use of wood fiber that threatens endangered forests.
End the clearing of natural forest ecosystems and their conversion into plantations for paper fiber.
Source any remaining virgin wood fibers for paper from independent, third–party certified forest managers that employ the most environmentally and socially responsible forest management and restoration practices (Forest Stewardship Council is the only acceptable international certification program that comes close to meeting this objective).
Use alternative crops for paper if comprehensive and credible analysis indicates that they are environmentally and socially preferable to other virgin fiber sources.
Eliminate widespread industrial use of pesticides, herbicides and fertilizers in plantations and fiber production.
Stop the introduction of paper fiber from genetically modified organisms
Maximize recycled content
Eliminate paper manufactured solely of virgin fiber and fundamentally reduce reliance on virgin tree fibers.
Maximize post-consumer recycled fiber content in all paper and paper products.
Increase the use of other recovered materials example agricultural residues and pre-consumer recycled as a fiber source in paper.

Based on www.greenamerica.org/PDF/PaperVision.pdf

Paper mills vary significantly in their environmental performance, depending on their age, efficiency and how they are run. Minimum-impact mills are those that minimize resource inputs (wood, water, energy and chemicals) and minimize the quantity and maximize the quality of releases to air, water and land (Axegard et al. 1997; Pryke 2008). Paper mills can optimize their environmental performance by implementing the

- most advanced manufacturing technologies,
- most efficient mill operations
- most effective environmental management systems.

The vision of Minimum Impact-Manufacturing has captured the imaginations of industry and the environmental community alike (Axegard et al. 1997; Pryke 2008). Minimum Impact-Mill is:

“A completely ecocyclic system for high quality pulp and paper production which efficiently utilizes the energy potential of the biomass”
“An ecologically sound industry, producing recyclable products from renewable resources”
“An industry we are so proud of we encourage our grand children to join”

There is an opportunity to move public perception from “the pulp and paper industry is the largest water consumer and biggest polluter” to “the pulp and paper industry is ecologically sound, while producing recyclable products from renewable resources.” However, public trust must be earned through addressing local issues like odor, plumes and other aesthetic issues. Elimination of elementary chlorine free bleaching (ECF) or totally chlorine free bleaching (TCF) bleaching effluent is not necessary for environmental protection, nor is it necessarily the place to start. Process development toward the minimum-impact mill should begin by concentrating on minimizing releases from the pulping and recovery processes. Presently, there are no kraft mills operating full time which completely recover all bleach plant effluent. In other words there are no “zero” effluent kraft mill bleach plants. The minimum-impact mill does not mean “no bleach plant effluent,” or “zero effluent,” nor is it exclusive to one bleaching technology. It is a much bigger concept (Hanninen 1996; Elo 1995). The minimum-impact mill is one which:

- Maximizes pulp yield and produces high quality products which can be easily recycled, and/or safely combustible
- Minimizes water consumption
- Minimizes wastes – gaseous, liquid and solid – and disposes of them optimally
- Maximizes the energy potential of the biomass
- Optimizes capital investment
- Creates sustainable value to shareholders, customers, employees and to local, regional, and national communities

The industry’s environmental progress over the last few decades, while maintaining economic viability provides confidence that the minimum-impact mill of the future will be realized. Several strategies have been proposed (Erickson 1995; Paper Task Force 1995; Maples et al. 1994; Ahlenius et al. 1994; Kinell et al. 1996; Wearing 1994; Albert 1993; Gleadow et al. 1996; Basta et al. 1996). These are:

- The Minimum-Impact Mill – MIM
- Minimum-Impact Manufacturing – MIM
- Bleach Filtrate Recovery – BFR®
- Closed Loop Bleaching – CLB
- The Eco-Balanced Pulp Mill
- Progressive Systems Closure
- Effluent Free
- Closed Cycle Technology
- Ecocyclic Pulp Mill
- Partial Mill Closure

A strong thrust within many of these process technology developments is toward recovery and elimination of bleach plant effluent. However, a direct link between bleaching processes and environmental responses of concern has not been demonstrated. Furthermore, current environmental research is pointing toward other processes within the mill, rather than bleaching, as the sources of substances causing environmental responses. In light of such information, some have questioned the wisdom of placing virtually exclusive emphasis on reduction or elimination of bleach plant effluent. They ask the following questions:

Where is the evidence that these technological developments will lead to reduced environmental impact?
Will new bleaching sequences complicate process chemistry?
Will demand for wood increase due to lower process yields?
Will energy consumption increase?
Will complicated and expensive control and back-up systems be required?

Finally there has been considerable debate as to compatibility and the merits of both ECF and TCF based bleaching strategies within minimum-impact manufacturing processes incorporating recycle and recovery of bleaching effluent.

Pressures to maximise energy efficiency, improve product quality, reduce environmental impact, and optimise capital and operating costs have significantly shaped the design of recent mills. Producers have responded to these demands by adopting efficient, low impact designs on economies of scale that far surpass most existing mills. Modern mills have less equipment, but are of much larger capacity than twentieth century mills (Johnson et al. 2009). New fibrelines have been built mainly in Asia and South America where access to fast growing raw material, other production cost advantages, stable politics and economies, and surging demand from the East give favourable levels of cost and return. India's non wood and hardwood market pulp segment must compete in the longer term with these new fibrelines.

Minimum environmental impact is not only to have nice quality control figures. It means a continuous effort in the direction of the zero impact. It is more difficult to achieve the objectives when you are closer to zero. However, this must be a philosophy, a conceptual way of working. With the rise in environmental awareness due to the lobbying by environmental organizations and with increased government regulation there is now a trend towards sustainability in the pulp and paper industry. During the last decade, there have been revolutionary technical developments in pulping, bleaching and chemical recovery technology. These developments have made it possible to further reduce loads in effluents and airborne emissions. Thus, there has been a strong progress towards minimum impact mills in the pulp and paper industry. The minimum-impact mill is a holistic manufacturing concept that encompasses environmental management systems, compliance with environmental laws and regulations and manufacturing technologies. The minimum impact mill is a much bigger concept which means that significant progress must be made in the following areas:

- Water Management
- Internal Chemical Management
- Energy Management
- Control and Discharge of Non-Process Elements
- Removal of Hazardous Pollutants

Sustainable pulp and paper manufacturing requires a holistic view of the manufacturing process. This concept begins with a vision and commitment to a long-term goal that should guide all decisions about the direction of both the mill operations and the selection of manufacturing technologies. Investing in manufacturing processes that prevent pollution and practicing good environmental management go hand-in-hand. A poorly run mill may not be able to reap the environmental benefits that result from installing advance pollution prevention technologies. Outdated manufacturing technologies, however, will limit the ability of a well run mill to achieve continuous environmental improvement. Adopting the long-term goal of operating minimum impact mills allows suppliers to develop measurable and cost effective investment strategies that provide environmental benefits and improve economic competitiveness. Pulp and paper mills routinely make investments in individual pieces of equipment and periodically undergo more costly renovations and expansions. The strategic application of the minimum impact mill concept will allow manufacturers to integrate decisions that affect manufacturing costs, productivity, quality and environmental impacts.

The minimum-impact mill is a dynamic and long-term goal that will require an evolution of technology in some cases. Many factors will affect the specific technology pathway and the rate at which individual mills will progress toward this goal. These factors include the products manufactured at the mill, the types of wood that are available, the mill's location, the age and configuration of equipment, operator expertise, the availability of capital and the stages a mill has reached in its capital investment cycle. Some mills, for example, will install the most advanced current technologies with a relatively low capital investment within the next 5 years.

Responsible pulp and paper operations can bring many benefits to forests, local economies and people, particularly in rural areas. Many pulp and paper companies are demonstrating leadership in responsible forestry and plantation management as well as in clean manufacturing processes and recycled content.

References

Ahlenius L, Alfthan CJ, Wikberg E (1994) Closing up a TCF bleach plant. In: CPPA 1994 international pulp bleaching conference proceedings, Vancouver, Canada, June 1994

Albert R (1993) Technical and economic feasibility of the effluent-free bleached kraft pulp mill. In: 1993 international non chlorine bleaching conference proceedings, Hilton Head, SC, USA, Mar 1993

Anslem EO, Oluighbo SN (2012) Mitigating the impact of climate change through waste recycling. Res J Environ Earth Sci 4(8):776–781

Axegard P, Carey J, Folke J, Gleadow P, Gullichsen J, Pryke DC, Reeve DW, Swan B, Uloth V (1997) Minimum-impact mills: issues and challenges. In: Proceedings of the minimum effluent mills symposium. Tappi Press, Atlanta, pp 529–541

Basta J, Wäne G, Herstad-Svärd S, Lundgren P, Johansson NG, Edwards L, Gu Y (1996) Partial closure in modern bleaching sequences. In: Tappi 1996 international pulp bleaching conference proceedings, Washington, DC, USA

Blazejczak J, Edler D (2000) Elements of innovation-friendly policy regimes – an international comparative study for the paper industry. In: Hemmelskamp J, Rennings K, Leone F (eds) Innovation-oriented environmental regulation: theoretical approaches and empirical analysis, vol 10, ZEW economic studies. Physica Verlag, Heidelberg/New York, pp 175–192

Elo A (1995) Minimum impact mill. In: Third global conference on paper and the environment, London, 26–28 March 1995, pp 105–110

Environmental Paper Network (2002) A common vision for transforming the paper industry: striving for environmental and social sustainability. 20 November 2002

Erickson D (1995) Closing up the bleach plant: striving for a minimum-impact mill. In: Tappi/NC state emerging pulping & bleaching technologies workshop, Raleigh, NC, USA, May 1995

Gielen D, Tam C (2006) Energy use, technologies and CO2 emissions in the pulp and paper industry. In: Energy efficient technologies and CO2 reduction potentials in the pulp and paper industry in collaboration with WBCSD, IEA, Paris, 9 October 2006

Gleadow P, Vice K, Johnson A, Sorenson D, Hastings C (1996) Mill applications of closed-cycle technology. In: Proceedings, 1996 international non-chlorine bleaching conference, March 1996

Hanninen E (1996) Minimum impact mill. Pap Asia 12(1):24–29

Johnson T, Johnson B, Gleadow P, Araneda H, Silva F, Aquilar R, Hsiang C (2009) 21st century fibrelines. Pulp Pap-Can 110(9):26–31

Kinell P, Ström K, Swan B (1996) Sustainable development in Stora pulp mills. In: Proceedings, 1996 international non-chlorine bleaching conference, March 1996

Lélé S (1991) Sustainable development: a critical review. World Dev 19(6):607–621

Low N, Gleeson B (2005) If sustainability is everything, maybe it's nothing? In: State of Australian cities conference, Griffith University, Brisbane, 30 November–2 December 2005, pp 01-1–01-10

Maples G, Ambady R, Caron JR, Stratton S, Vega Canovas R (1994) BFR: a new process toward bleach plant closure. TAPPI J 77(11):71–80

Marcuse P (1998) Sustainability is not enough. Environ Urban 10(2):103–111

Mawhinney M (2002) Sustainable development: understanding the green debates. Blackwell Publishing, Oxford

OECD (2001) Environmental outlook. OECD, Paris, p 215

Ogunwusi AA, Ibrahim HD (2014) Advances in pulp and paper technology and the implication for the paper industry in Nigeria. Ind Eng Lett 4(10):17–29. ISSN 2224–6096 (Paper), ISSN 2225–0581

Paper Task Force (1995) Paper task force recommendations for purchasing and using environmentally preferable paper, Environmental Defense Fund, 15 December 1995

Pryke D (2008) Perspectives on the pulp and paper industry. Digital Presentation

Reinstaller A (2005) Policy entrepreneurship in the co-evolution of institutions, preferences, and technology. Comparing the diffusion of totally chlorine free pulp bleaching technologies in the US and Sweden. Res Policy 34(9):1366–1384

RISI (2014) Global paper and board production hits record levels in 2013. In: Annual review of pulp and paper statistics. www.risiinfo.com/…/news/…/Global-paper-and-board-production-hits-re

Sridach W (2010) The environmentally benign pulping process of non wood fibres. Suranaree J Sci Technol 17(2):105–123

Sustainable Manufacturing Initiative (2011) www.csiro.au/…/CSIROau/…/What%20is%20Sustainable%20Manufactur

Sutton P (2004) A perspective on environmental sustainability? Victorian Commissioner for Environmental Sustainability, Melbourne

Toepfer K (2002) Keynote address. In: UNEP's 7th international high level seminar on cleaner production, 29–30 April 2002

UN General Assembly (1987) Towards sustainable development, Annex to document A/42/427, Environment: our common future. In: Report of the World commission on environment and development: our common future. Available at http://www.un-documents.net/ocf-02.htm

Wearing J (1994) Closed cycle design in the pulp and paper industry: current technology and needs for future research. In: Presentation to France-Canada exchange on the paper industry and the environment. Niagara-on-the-Lake, ON, October 1994. www.greenamerica.org/PDF/PaperVision.pdf

Chapter 2
Basic Overview of Pulp and Paper Manufacturing Process

Abstract Pulp and paper mills are highly complex and integrate many different process areas including wood preparation, pulping, chemical recovery, bleaching, and papermaking to convert wood to the final product. Processing options and the type of wood processed are often determined by the final product.

The pulp for papermaking may be produced from virgin fibre by chemical or mechanical means or may be produced by the repulping of paper for recycling. Wood is the main original raw material. Paper for recycling accounts for about 50 % of the fibres used – but in a few cases straw, hemp, grass, cotton and other cellulose-bearing material can be used. 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 fibres 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. Post-use, an increasing fraction of paper and paper products is recycled. Non recycled paper is either landfilled or incinerated.

Keywords Pulp and Paper industry • Pulping • Bleaching • Papermaking • Recycling • Chemical recovery

The pulp and paper industry is one of the most important industries in the world. It supplies paper to over 5 billion people worldwide. Originally, papermaking was a slow and labour-intensive process. Today pulping and papermaking are driven by capital-intensive technical equipment and high-tech and high-speed paper machines that produce rolls of paper at a speed that may reach 2000 m/min. and with a web width that may exceed 8 m. Paper is essentially a sheet of cellulose fibres with a number of added constituents, when necessary, to affect the quality of the sheet and its fitness for the intended end use. The two terms paper and board generally refer to the weight of the product sheet (grammage) with paper ranging up to about 160 or 220 g/m^2 and a heavier sheet regarded as board (cartonboard). The grammage above which papers are called board however vary slightly between countries.

AD 105 is often cited as the year in which papermaking was invented. In that year, historical records show that the invention of paper was reported to the Chinese Emperor by Ts'ai Lun, an official of the Imperial Court. The modem manufacture

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of paper evolved from an ancient art first developed in China. Although the modern product differs considerably from its ancestral materials, papermaking retains distinct similarities to the processes developed by Ts'ai Lun. In principle, paper is made by:

- Pulping, to separate and clean the fibres
- Beating and refining the fibres
- Diluting to form a thin fibre slurry
- Suspended in solution
- Forming a web of fibres on a thin screen
- Pressing the web to increase the density of the material
- Drying to remove the remaining moisture
- Finishing, to provide a suitable surface for the intended end use.

Pulp and paper are made from cellulosic fibres and other plant materials, although some synthetic materials may be used to impart special qualities to the finished product. Most paper is made from wood fibres, but rags, flax, cotton linters, and bagasse which is a sugar cane residue are also used in some papers. Used paper is also recycled, and after purifying and sometimes deinking, it is often mixed with virgin fibres and reformed again into paper. Other products made from wood pulp (cellulose) include diapers, rayon, cellulose acetate, and cellulose esters, which are used for cloth, packaging films, and explosives. Wood is composed of cellulose, lignin, hemicellulose, and extractives. Cellulose, comprises about 50 % of wood by oven dry weight. This constituent is of primary interest in papermaking. Lignin cements the wood fibres together. It is a complex organic chemical. Its structure and properties are not fully understood. It is largely burned for the generation of energy used in pulp and paper mills. As the chemistry of lignin becomes better understood, what is now mostly a waste product used for fuel (some is converted to chemical products), it could become a valuable feed stock for new chemical products. The objective of pulping process is to remove as much lignin as possible without sacrificing fibre strength, thereby freeing the fibres and removing impurities which cause discoloration and possible future disintegration of the paper. Hemicellulose plays an important role in fibre-to-fibre bonding in papermaking. Several extractives (example, oleoresins and waxes) are contained in wood but do not contribute to its strength properties; these too are removed during the pulping process. The fibre from nearly any plant or tree can be used for paper. However, the strength and quality of fibre, and other factors that can complicate the pulping process, varies among tree species. In general, the softwoods (example, pines, firs, and spruces) yield long and strong fibres that impart strength to paper and are used for boxes and packaging. Hardwoods, on the other hand, generally have shorter fibres and therefore produce a weaker paper, but one that is smoother, more opaque, and better suited for printing. Both softwoods and hardwoods are used for papermaking and are sometimes mixed to provide both strength and printability to the finished product. Figure 2.1 shows an overview of the pulping and papermaking process.

The manufacturing of paper or paperboard can be divided into several process areas (Table 2.1). Paper production is mainly a two-step process in which a fibrous

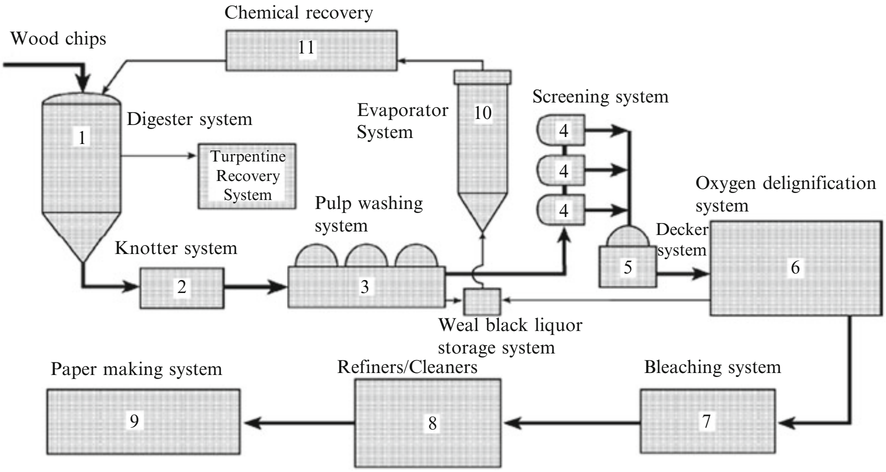

Fig. 2.1 Overview of kraft pulping mill with papermaking system. Based on USEPA (1998)

Table 2.1 Steps involved in the manufacturing of pulp and paper

Operation	Processes
Raw material preparation	Debarking
	Chipping and conveying
Pulping	Chemical pulping
	Semichemical pulping
	Mechanical pulping
	Recycled paper pulping
Chemical recovery	Evaporation
	Recovery Boiler
	Recausticizing
	Calcining
Bleaching	Mechanical or chemical pulp bleaching
Stock preparation and papermaking	Preparation of stock
	Dewatering
	Pressing and drying
	Finishing

raw material is first converted into pulp, and then the pulp is converted into paper. The harvested wood is first processed so that the fibres 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. Post-use, an increasing fraction of paper and paper products is recycled. Nonrecycled paper is either landfilled or incinerated.

Some integrated pulp and paper mills perform multiple operations (example, chemical pulping, bleaching, and papermaking; pulping and unbleached papermaking etc.). Nonintegrated mills may perform either pulping (with or without bleaching), or papermaking (with or without bleaching).

2.1 Raw Material Preparation

Wood is the primary raw material used to manufacture pulp, although other raw materials can be used. Pulp manufacturing starts with raw material preparation, which includes debarking (when wood is used as raw material), chipping, chip screening, chip handling and storage and other processes such as depithing (for example, when bagasse is used as the raw material) (Biermann 1996; Gullichsen 2000; Ressel 2006). Wood typically enters a pulp and paper mill as logs or chips and is processed in the wood preparation area, referred to as the woodyard. In general, woodyard operations are independent of the type of pulping process. If the wood enters the woodyard as logs, a series of operations converts the logs into a form suitable for pulping, usually wood chips. Logs are transported to the slasher, where they are cut into desired lengths, followed by debarking, chipping, chip screening, and conveyance to storage. The chips produced from logs or purchased chips are usually stored on-site in large storage piles. Chips are screened for size, cleaned, and temporarily stored for further processing (Smook 1992).

Certain mechanical pulping processes, such as stone groundwood pulping, use roundwood; however, the majority of pulping operations require wood chips. A uniform chip size (typically 20 mm long in the grain direction and 4 mm thick) is necessary for the efficiency of the processes and for the quality of the pulp. The chips are then put on a set of vibrating screens to remove those that are too large or small. Large chips stay on the top screens and are sent to be re-cut, while the smaller chips are usually burned with the bark or may be sold for other purposes. Non-wood fibres are handled in ways specific to their composition in order to minimize degradation of the fibres and thus maximize pulp yield. Non-wood raw materials are usually managed in bales.

Two main products derive from debarking process, the chips which are the main product and the bark that can be characterized as by-product. Bark can be used as a fuel or it can be sold off-site for other purposes. Bark is typically used as a fuel in burners for energy production. Other debarking methods that are being used are the following (Ressel 2006):

- Rotary or cradle debarker
- Ring debarker
- Flail debarker
- Rosser head debarker
- Mobile debarker

After the logs have been debarked, the chipping of the logs occurs in order to reduce logs size and produce chips; a typical option for chipping is the use of a radial chipper. The quality of the chips is of high importance, since if the chips produced are not homogeneous, raw material consumption will increase. Furthermore, a homogenized chip distribution will improve the energy performance of the system. The next process is the screening of the produced chips in order to separate long size chips that are not properly chipped; the screening process also contributes by removing sawdust. The recovered sawdust is also a by-product that can be burnt while the long size chips can be re-chipped in a crusher or re-chipper. The screening process can affect the plant's performance. Optimizing the screening process can lead to the production of high-quality pulp and can improve the environmental performance of the mill by reducing pollution. In order to achieve the optimum screening performance however, raw material consumption should be increased. Chips produced can now be transported to the next step which is pulping. Chips transportation is made using conveyors. Various types of conveyors exist (Ressel 2006) which are listed below:

- Chain conveyor
- Roller conveyor
- Steel plate conveyor
- Vibrating conveyor
- Belt conveyor
- Scraper conveyor
- Screw conveyor

Storage facilities may be required for storing materials or products in some cases; both raw material (wood) and chips produced may demand storage. Storage conditions are very much important in cases where the material needs to be transported.

2.2 Pulping

During the pulping process, wood chips are separated into individual cellulose fibres by removing the lignin from the wood (Smook 1992; Biermann 1996; Ince 2004). Table 2.2 shows the main types of pulping processes.

2.2.1 Chemical Pulping

Chemical pulping (i.e., kraft, soda, and sulphite) involves "cooking" of raw materials (example, wood chips) using aqueous chemical solutions and elevated temperature and pressure to extract pulp fibres. Chemical pulps are made by cooking the raw materials, using the kraft (sulphate) and sulphite processes (Casey 1983a).

Table 2.2 Types of pulping

Pulp grades	Raw material	End product use
Chemical pulps		
Sulfite pulp	Softwoods and hardwoods	Fine and printing papers
Kraft sulfate pulp	Softwoods and hardwoods	Bleached-printing and writing papers, paperboard, unbleached-heavy packaging papers, paperboard
Dissolving pulp	Softwoods and hardwoods	Viscose rayon, cellophane, acetate fibers, and film
Semichemical pulps		
Cold-caustic process	Softwoods and hardwoods	Newsprint and groundwood printing papers
Neutral sulfite process	Hardwoods	Newsprint and groundwood printing papers
Mechanical pulps		
Stone groundwood	Mainly softwoods	Corrugating medium
Refiner mechanical (RMP)	Mainly softwoods	Newsprint and groundwood printing papers
Thermomechanical (TMP)	Mainly softwoods	Newsprint and groundwood printing papers
Chemi-mechanical (CTMP)	Mainly softwoods	Newsprint, Fine Papers

Kraft pulping is by far the most common pulping process used by plants in the United States for virgin fibre, accounting for more than 80 % of total United States pulp production.

2.2.1.1 Kraft Pulping Process

Kraft process produces a variety of pulps. These pulps are used mainly for packaging and high-strength papers and board. 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. The kraft pulping process uses an alkaline cooking liquor of sodium hydroxide and sodium sulphide to digest the wood, while the similar soda process uses only sodium hydroxide. This cooking liquor (white liquor) is mixed with the wood chips in a reaction vessel (digester). After the wood chips have been "cooked," the contents of the digester are discharged under pressure into a blow tank. As the mass of softened, cooked chips impacts on the tangential entry of the blow tank, the chips disintegrate into fibres or "pulp." The pulp and spent cooking liquor (black liquor) are subsequently separated in a series of brown stock washers (EPA 2001a). A number of pulp grades are commonly produced, and the yield depends on the grade of product. Unbleached pulp grades are characterized by a dark brown color. These are generally used for packaging products and are cooked to a higher yield and retain more of the original lignin. Bleached pulp grades are used to produce 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 (MCC, ITC and Compact Cooking as examples for continuous cooking and Coldblow, Superbatch/RDH and Continuous Batch Cooking, CBC, for batch cooking technology) have emerged through continuous research and development (Annergren and Lundqvist 2008; Marcoccia et al. 2000).

2.2.1.2 Sulphite Process

The cooking liquor in the sulphite pulping process is an acidic mixture of sulfurous acid and bisulphite ion. In preparing sulphite cooking liquors, cooled sulfur dioxide gas is absorbed in water containing one of four chemical bases – magnesium, ammonia, sodium, or calcium. The sulphite pulping process uses the acid solution in the cooking liquor to degrade the lignin bonds between wood fibres. Sulphite pulps have less color than kraft pulps and can be bleached more easily, but are not as strong. The efficiency and effectiveness of the sulphite process is also dependent on the type of wood furnish and the absence of bark. Due to these reasons, the use of sulphite pulping has declined in comparison to kraft pulping over time (EPA 2001a). This process uses different chemicals to attack and remove lignin. Sulphite 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 sulphite process is usually intolerant of resinous softwoods, tannin-containing hardwoods, and any furnish containing bark. Sulphite 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 sulphite process is characterised 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. The dominating sulphite pulping process in Europe is the magnesium sulphite pulping with some mills using sodium as base. Both magnesium and sodium bases allow chemical recovery. The lignosulphonates generated in the cooking liquour can be used as a raw material for producing different chemical products.

2.2.2 Mechanical Pulping

There are three main categories of mechanical pulp: groundwood pulp, refining pulp, and chemi-mechanical pulp. In both the grinding and refining processes, the temperature is increased to soften the lignin. This breaks the bonds between the fibres (Gullichsen 2000; Casey 1983b). Groundwood pulp shows favorable properties with respect to brightness (≥85 % 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 (example, 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 (Arppe 2001). The most important refiner mechanical pulping process today is thermomechanical pulping (TMP). This involves high-temperature steaming before refining; this softens the inter-fibre lignin and causes partial removal of the outer layers of the fibres, thereby baring cellulosic surfaces for inter-fibre 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 fibres 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 sulphite prior to refining causes partial sulfonation of middle lamella lignin. The better swelling properties and the lower glass transition temperature of lignin results in easier liberation of the fibres in subsequent refining. The chemithermomechanical pulp (CTMP) show good strength properties, even when using hardwood as a fibre 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 fibre material. It is anticipated that mechanical paper will consolidate its position as one major fibre 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 fibre will put pressure on the growth in mechanical pulp volumes.

2.2.3 Semi-chemical Pulping

Semi-chemical pulping uses a combination of chemical and mechanical (i.e., grinding) energy to extract pulp fibres. Wood chips first are partially softened in a digester with chemicals, steam, and heat. Once chips are softened, mechanical methods complete the pulping process. The pulp is washed after digestion to remove cooking liquor chemicals and organic compounds dissolved from the wood chips. This virgin pulp is then mixed with 20–35 % recovered fibre (example, double-lined kraft clippings) or repulped secondary fibre (example, old corrugated containers) to enhance machinability. The chemical portion (example, cooking liquors, process equipment) of the pulping process and pulp washing steps are very similar to kraft and sulphite processes. At currently operating mills, the chemical portion of the semi-chemical pulping process uses either a nonsulfur or neutral sulphite semi-chemical (NSSC) process. The nonsulfur process uses either sodium carbonate only or mixtures of sodium carbonate and sodium hydroxide for cooking the wood chips, while the NSSC process uses a sodium-based sulphite cooking liquor (EPA 2001a). Semichemical pulps, which apply to the category of chemical pulps, are obtained mainly from hardwoods in yields of between 65 and 85 % (average ca. 75 %). The most important semichemical process is the NSSC process, in which chips undergo partial chemical pulping using a buffered sodium sulphite solution, and are then treated in disc refiners to complete the fibre separation. The sulfonation of mainly middle lamella lignin causes a partial dissolution so that the fibres 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, as well as 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 sulphite spent liquor is processed together with the kraft liquor. The sulphite spent liquor then provides the necessary make-up (Na, S) for the kraft process. However, with the greatly improving recovery efficiency of modern kraft mills, the NSCC make-up is no longer needed so that high-yield kraft pulping develops as a serious alternative to NSCC cooking. Semichemical pulps is still an important product category, however, and account for 3.9 % of all virgin fibre material.

2.2.4 Secondary Fibre Pulping

Recovered paper has become an increasingly important source of fibre for papermaking (Bajpai 2013). Currently, nearly 50 % of the fibre raw material for papermaking is based on recycled fibre. In the recycling process, recycled paper or paperboard is rewetted and reduced to pulp, principally by mechanical means. Inks, adhesives, and other contaminants may be removed by chemical deinking and mechanical separation. Because the fibres in recycled paper and paperboard have been fully dried and then rewetted, they generally have different physical properties than virgin wood pulp fibres. In some cases, mills using recycled paper, without deinking, can operate without any effluent discharge due to the use of closed water cycles together with small anaerobic or aerobic biological treatment systems to remove some dissolved organics from the recycled waters. The closed cycle processes are practical where the product can tolerate a certain degree of dirt and contamination, as in some packaging and construction paper grades. In some recycle plants, approximately 30–40 % of the raw material processed results in sludge that requires management as a solid waste. Processing of recovered paper without deinking is sufficient for applications that do not require high brightness, such as corrugated board, carton board, and some tissue. Deinking processes are used to remove ink to make the pulp brighter and cleaner. Sometimes bleaching is also applied after deinking. Recycled fibre with deinking is used for applications requiring higher brightness, such as newsprint, magazine paper, and tissue. Process waters are similar to those from systems without deinking. However, deinking results in lower yields and requires additional internal treatment. The pulp yield may be as low as 60–70 % of the recovered paper entering the process; therefore, as much as 30–40 % of the entering material may enter the white water and need to be treated and removed before discharge of the wastewater.

2.2.5 Dissolving Kraft and Sulphite Pulping Processes

Dissolving kraft and sulphite pulping processes are used to produce highly bleached and purified wood pulp suitable for conversion into products such as rayon, viscose, acetate, and cellophane (EPA 2002).

2.2.6 Non-wood Pulping

Worldwide, non-wood sources make up about 6 % of the total fibre supply for papermaking. Non-wood fibres are derived from agricultural fibres such as straw and other plant fibres such as bamboo, bagasse, and annual fibre crops such as kenaf (Ince 2004). In general, non-wood plant fibres are more costly to collect and process than wood fibre in regions of the world where wood supplies are adequate, and thus pulp is produced almost exclusively from wood fibre in most regions of the world. However, substantial quantities of nonwood pulp are produced, especially in regions of Asia and Africa where wood fibre is relatively less abundant and non-wood fibres are available. Most non-wood fibres are relatively short, similar to fibres derived from hardwood, and therefore are suited to similar applications, such as writing paper. However, non-wood fibres are often used for other grades as well, such as newsprint and corrugated board, simply because local wood is not available for pulping. Non-wood species normally cook more readily than wood chips. Thus, Kraft cooking is normally replaced with soda cooking (sodium hydroxide only), and the charge is usually less. The spent liquors usually have lower concentrations of dissolved organics and process chemicals compared with chemical pulping of wood, thus increasing the cost of chemical recovery. In addition, non-wood pulping plants are normally small, typically producing less than 100,000 t/year of pulp, and therefore lack the economies of scale that make environmental investments economical at larger facilities. As a result, many non-wood mills have limited or no recovery of chemicals and have substantially higher waste emissions per ton of product than modern Kraft mills. Non-wood plants normally contain higher amounts of silica than wood. Silica causes problems in chemical recovery and also adversely affects paper quality. In particular, silica increases scaling in the liquor evaporators and reduces the efficiency of both the causticizing operation and conversion of lime mud (calcium carbonate) to calcium oxide (burnt lime) in the lime kiln. To counter these affects, non-wood pulping facilities generally discharge higher proportions of lime mud and purchase higher amounts of lime or limestone as make-up. In the United States, non-wood fibre pulp production is not common (EPA 2001b).

2.3 Pulp Washing

The purpose of pulp washing is to obtain pulp that is free of unwanted solubles. In the most basic case, this can be done by replacement of the contaminated liquor accompanying the pulp fibres by clean water. In a modern pulp mill, washing operations include also displacement of one type of liquor by another type of liquor. Aside from its washing function, washing equipment must at times also allow the effective separation of chemical regimes or temperature levels between single fibreline process steps (Krotscheck 2006). Various benefits result from pulp washing, such as:

- Minimizing the chemical loss from the cooking liquor cycle
- Maximizing recovery of organic substances for further processing or incineration
- Reducing the environmental impact of fibreline operations
- Limiting the carry-over between process stages
- Maximizing the re-use of chemicals and the energy conservation within a single bleaching stage
- Obtaining a clean final pulp product

Ideally, pulp washing is carried out with the minimum amount of wash water in order to conserve fresh water resources and to take capacity burden from downstream areas which process the wash filtrate. Very often, pulp washing is a compromise between the cleanness of the pulp and the amount of wash water to be used. In the mill, pulp washing operations can be found in brownstock washing, in the bleach plant and, as the case may be, also in digesting and on the dewatering machine (Smook 1992; Krotscheck 2006).

After pulp production, pulp is processed to remove impurities, such as uncooked chips, and recycles any residual cooking liquor via the pulp washing process (Smook 1992). Pulps are processed in a wide variety of ways, depending on the method that generated them (e.g., chemical, sulphite). 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 of time, 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 sulphite. Efficient washing is very important 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 (example, dioxins, 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, hydro-cyclone, or centri-cleaning) 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).

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 for 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 obtain 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 before to burning the liquor in the recovery furnace. This is a costly process and often the bottleneck in pulp mill operations. Reducing the use of wash water will therefore reduce the steam cost for evaporation. In dilution/extraction washing, the pulp slurry is diluted and mixed with weak wash liquor or fresh water. 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 fibres.

All pulp washing equipment is based on one of 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 utilizes dilution\extraction. Most pulp washing systems consist of more than one washing stage. The highest washing efficiency would be achieved if fresh water 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 counter-current washing, the pulp in the final stage is washed with the cleanest available wash water or fresh water before leaving the system. The drained water from this stage is then sent backwards through each of the previous stages in a direction opposite to the pulp flow (Smook 1992).

2.4 Pulp Screening, Cleaning and Fractionation

Screening of the pulp is done to remove oversized and unwanted particles from good papermaking fibres so that the screened pulp is more suitable for the paper or board product in which it will be used (Biermann 1996; Ljokkoi 2000; Krotscheck 2006). 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. In low-yield pulps they are removed in special coarse screens called knotters.

The main purpose of fine screening is to remove shives. Shives are small fibre bundles that have not been separated by chemical pulping or mechanical action. Chop is another kind of oversize wood particle removed in screening. It is more of a problem when pulping hardwoods, since 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.

2.5 Bleaching

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 (Bajpai 2012). Bleaching is any process that chemically alters pulp to increase its brightness. Bleached pulps create papers that are whiter, brighter, softer, and more absorbent than unbleached pulps. Bleached pulps are used for products where high purity is required and yellowing is not desired (example printing and writing papers). Unbleached pulp is typically used to produce boxboard, linerboard, and grocery bags. Any type of pulp may be bleached, but the type(s) of fibre and pulping processes used, as well as the desired qualities and end use of the final product, greatly affect the type and degree of pulp bleaching possible. The lignin content of a pulp is the major determinant of its bleaching potential. Pulps with high lignin content (example, mechanical or semi-chemical) are difficult to bleach fully and require heavy chemical inputs. Excessive bleaching of mechanical and semi-chemical pulps results in loss of pulp yield due to fibre destruction. Chemical pulps can be bleached to a greater extent due to their low (10 %) lignin content. Whereas delignification can be carried out within closed water systems, bleach plants tend to discharge effluent to external treatment. Effluents from the bleach plant cannot easily be recirculated into the chemicals recovery mainly because they would increase the build-up of chlorides and other unwanted inorganic elements in the chemical recovery system, which can cause corrosion, scaling, and other problems.

For chemical pulps an important benefit is the reduction of fibre bundles and shives as well as the removal of bark fragments. This improves the cleanliness of the pulp. Bleaching also eliminates the problem of yellowing of paper in light, as it removes the residual lignin in the unbleached pulp. Resin and other extractives present in unbleached chemical pulps are also removed during bleaching, and this improves the absorbency, which is an important property for tissue paper grades. In the manufacture of pulp for reconstituted cellulose such as rayon and for cellulose derivatives such as cellulose acetate, all wood components other than cellulose must be removed. In this situation, bleaching is an effective purification process for removing hemicelluloses and wood extractives as well as lignin. To achieve some of these product improvements, it is often necessary to bleach to high brightness. Thus, high brightness may in fact be a secondary characteristic of the final product and not the primary benefit. It is therefore simplistic to suggest that bleaching to lower brightness should be 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 fibre flexibility and strength. On the other hand, a lowered hemicellulose content results in a lower swelling potential of the fibres and a reduced bonding ability of the fibre surfaces. If bleaching conditions are too severe there will be fibre damage, leading to a lower strength of the paper. The purpose of bleaching is to dissolve and remove the lignin from wood to bring the pulp to a desired brightness level (Reeve 1989, 1996a; Farr et al. 1992; Fredette 1996; McDonough 1992). Bleaching is carried out in a multi-stage process that alternate delignification and dissolved material extracting stages. Additional oxygen- or hydrogen peroxide-based delignification may be added to reinforce the extracting operation. Since its introduction at the turn of the century, chemical Kraft bleaching has been refined into a stepwise progression of chemical reaction, evolving from a single-stage hypochlorite (H) treatment to a multi-stage process, involving chlorine (CI_2), chlorine dioxide (CIO_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 1989, 1996a, b).

The introduction of chlorine and chlorine dioxide in the 1930s and early 1940s, respectively, increased markedly the efficiency of the bleaching process (Rapson and Strumila 1979; Reeve 1996a; Fredette 1996). Being much more reactive and selective than hypochlorite, chlorine 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 multi-stage 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, example improved pulp and chemical mixing, multiple splitted chlorine additions, and pH adjustments increased the economics of the process and led to significant reduction of wastewater (McDonough 1992, 1995; Malinen and Fuhrmann 1995). In addition, higher chlorine dioxide substitution, brought down significantly the generation and release of harmful chlorinated organic compounds.

Concerns over chlorinated compounds such as dioxins, furans, and chloroform have resulted in a shift away from the use of chlorinated compounds in the bleaching process. Bleaching chemicals are added to the pulp in stages in the bleaching towers. Spent bleaching chemicals are removed between each stage in the washers. Washer effluent is collected in the seal tanks and either re-used in other stages as wash water or sent to wastewater treatment.

Bleaching of mechanical pulp is based on lignin-saving methods and is fundamentally different from bleaching of chemical pulps, which is based on removal of lignin. The bleaching of mechanical pulp changes chromophoric groups of lignin polymers into a colorless form. Thus, the bleaching of mechanical pulp increases primarily the brightness of the pulp with minimum losses of dry solids and overall yield. The effect is not permanent, and the paper yellows with time. As it does not result in permanent brightness gain, bleached mechanical pulp is more suitable for newsprint and magazine paper than for books or archive papers. The lignin- saving bleaching is carried out in one to two stages, depending on the final brightness requirements of the pulp. The bleaching stages are distinguished according to the bleaching agent applied. Reductive bleaching uses sodium dithionite, which does not dissolve organic material from the pulp, and therefore results in only a minimal reduction in yield. Residual dithionite in the pulp can cause corrosion of metallic components downstream in the process. In most mills a metal chelating agent (example Ethylenediaminetetraacetic acid (EDTA), diethylene triamine pentaacetic acid (DTPA)) is used to prevent degradation of the dithionite. Oxidative bleaching uses hydrogen peroxide. Peroxide bleaching results in an approximately 2 % reduction in yield, mainly due to the alkalinity during the bleaching that results in some dissolution of organic substances in the wood (and in an increase of pollution load). Peroxide bleaching also improves the strength and water uptake capacity of the pulp. The bleaching process results in lower brightness in the presence of heavy metal ions; therefore, chelating agents (example EDTA, DTPA) are usually added before bleaching to form complexes with heavy metals (example Fe, Mn, Cu, Cr), which prevents the pulp from discoloring and the peroxide from decomposing. EDTA and DTPA contain nitrogen, which enters the wastewater. Introduction of a washing stage between pulping and bleaching is effective in reducing the problematic metals and can thus reduce the amount of chelating agent needed and improve the effectiveness of the applied peroxide. The bleached pulp is acidified with sulfuric acid or sulfur dioxide to a pH of 5–6.

2.6 Chemical Recovery

For economic and environmental reasons, chemical and semi-chemical pulp mills employ chemical recovery processes to reclaim spent cooking chemicals from the pulping process (Vakkilainen 2000; Tran 2007; Reeve 2002). At Kraft and soda pulp mills, spent cooking liquor, referred to as "weak black liquor," from the brown stock washers is routed to the chemical recovery area at kraft and soda pulp mills (Bajpai 2008). The chemical recovery process involves concentrating weak black liquor, combusting organic compounds, reducing inorganic compounds, and reconstituting the cooking liquor. The typical kraft chemical recovery process consists of the general steps described in the following paragraphs (EPA 2001a).

2.6.1 Black Liquor Concentration

Residual weak black liquor from the pulping process is a dilute solution (approximately 12–15 % solids) of wood lignins, organic materials, oxidized inorganic compounds (sodium sulphate, sodium carbonate), and white liquor (sodium sulphide and sodium hydroxide). The weak black liquor is first directed through a series of multiple-effect evaporators to increase the solids content to about 50 % to form "strong black liquor." The strong black liquor from the multiple-effect evaporators system is either oxidized in the black liquor oxidation system if it is further concentrated in a direct contact evaporator or routed directly to a nondirect contact evaporator, also called a concentrator. Oxidation of the black liquor before evaporation in a direct contact evaporator reduces emissions of odorous total reduced sulfur compounds, which are stripped from the black liquor in the direct contact evaporator when it contacts hot flue gases from the recovery furnace. The solids content of the black liquor following the final evaporator/ concentrator typically averages 65–68 %. The soda chemical recovery process is similar to the kraft process, except that the soda process does not require black liquor oxidation systems, since it is a nonsulfur process that does not result in total reduced sulfur emissions.

2.6.2 Recovery Furnace

The concentrated black liquor is then sprayed into the recovery furnace, where organic compounds are combusted, and the sodium sulphate is reduced to sodium sulphide (Vakkilainen 2000; Tran 2007). The black liquor burned in the recovery furnace has a high energy content (5,800–6,600 British thermal units per pound

[Btu/lb] of dry solids), which is recovered as steam for process requirements, such as cooking wood chips, heating and evaporating black liquor, preheating combustion air, and drying the pulp or paper products. The process steam from the recovery furnace is often supplemented with fossil fuel-fired and/or wood-fired power boilers. Particulate matter (primarily sodium sulphate) exiting the furnace with the hot flue gases is collected in an electrostatic precipitator (ESP) and added to the black liquor to be fired in the recovery furnace. Additional makeup sodium sulphate, or "saltcake," may also be added to the black liquor prior to firing. Molten inorganic salts, referred to as "smelt," collect in a char bed at the bottom of the 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 sodium sulphide and sodium carbonate. Green liquor also contains insoluble unburned carbon and inorganic impurities, called dregs, which are removed in a series of clarification tanks.

2.6.3 Causticizing and Calcining

Decanted green liquor is transferred to the causticizing area, where the sodium carbonate is converted to sodium hydroxide by the addition of lime (calcium oxide). The green liquor is first transferred to a slaker tank, where calcium oxide from the lime kiln reacts with water to form calcium hydroxide (Biermann 1996; Adams 1992; Venkatesh 1992). From the slaker, liquor flows through a series of agitated tanks, referred to as causticizers, that allow the causticizing reaction to go to completion (i.e., calcium hydroxide reacts with sodium carbonate to form sodium hydroxide and calcium carbonate). The causticizing product is then routed to the white liquor clarifier, which removes calcium carbonate precipitate, referred to as "lime mud." The lime mud is washed in the mud washer to remove the last traces of sodium. The mud from the mud washer is then dried and calcined in a lime kiln to produce "reburned" lime, which is reintroduced to the slaker. The mud washer filtrate, known as weak wash, is used in the SDT to dissolve recovery furnace smelt. The white liquor from the clarifier is recycled to the digesters in the pulping area of the mill (Arpalahti et al. 2000).

2.7 Stock Preparation and Papermaking

Stock preparation involves a series of operations by which pulp properties are tailored to fit the product produced. To balance the efficiency and reliability of the papermaking process against end-product quality is a crucial factor in stock preparation optimization. The objective of fibre stock preparation systems is to modify the different ingoing raw materials in such a way that the finished stock finally supplied to the paper machine suits the requirements of the paper machine and of the quality demands put on the produced paper or board. The raw stocks used are the

Table 2.3 Unit processes in stock preparation

Unit process	Objective
Slushing and deflaking	To break down the fiber raw material into a suspension of individual fibers. Slushing should at least result in a pumpable suspension enabling coarse separation and deflaking if required
	In the case of recovered paper, ink particles and other nonpaper particles should be detached from the fibers
Screening	To separate particles from the suspension which differ in size, shape and deformability from the fibers
Fractionation	To separate fiber fractions from each other according to defined criteria such as size or deformability of the fibers
Centrifugal cleaning	To separate particles from the suspension which differ in specific gravity, size and shape from the fibers
Refining	To modify the morphology and surface characteristics of the fibers
Selective flotation	To separate particles from the suspension which differ in surface properties (hydrophobicity) from the fibers
Nonselective flotation	To separate fine and dissolved solids from water
Bleaching	To impart yellowed or brown fibers with the required brightness and luminance
Washing	To separate fine solid particles from suspension (solid/solid separation)
Dewatering	To separate water and solids
Dispersing	To reduce the size of dirt specks and stickies (visibility, floatability), to detach ink particles from fibers

Based on Holik (2006)

various types of virgin pulps as well as recovered paper grades (Biermann 1996; Paulapuro 2000). They are available in the form of bales, loose material or, in the case of integrated mills, as suspensions. The finished stock is a suspension of defined quality as far as the mixture and characteristics of the fibres, additives, and impurities are concerned. This quality essentially determines paper machine runnability and is the basis for the final paper and board quality. Stock preparation consists of several process steps (Table 2.3). 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 are omitted. The operations are practiced in the paper mills are Dispersion; Refining and Metering and blending of fibre and additive. A number of new concepts have been introduced by Kadant Lamort with regard to virgin pulp stock preparation.

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 fibres and reduce any flakes into individual fibres.

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 fibres 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 fibres. 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 fibre properties in different ways for specific grades of paper. Usually, it aims to develop the bonding ability of the fibres without reducing their individual strength by damaging them too much, while minimising the development of drainage resistance. So the refining process is based on the properties required in the final paper. Different types of fibre react differently because of differences in their morphological properties (Baker 2000, 2005). The refining process must take into account the type of fibres.

Most of the strength properties of paper increase with pulp refining, since they rely on fibre-fibre bonding. However, the tear strength, which depends highly on the strength of the individual fibres, decreases with refining. After a certain point the factor limiting the strength is not the fibre-fibre bonding, but the strength of the individual fibres. Refining beyond this causes a decrease in other strength properties besides tear. Refining a pulp increases the fibres' 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 fibre 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 fibre clumps caught between the bar-to-bar surfaces. During beating and refining, fibres randomly and repeatedly undergo tensile, compressive, shear and bending forces. They respond in three ways (Bajpai 2005; Baker 2000, 2005; Stevens 1992):

- Fibres develop new surfaces externally through fibrillation and internally through fibre wall delamination.
- Fibres deform, resulting in changes in their geometric shape and the fibrillar alignment along their length. Overall, the fibres flatten or collapse. Fibre curl changes and kinks are induced or straightened. On the small scale, dislocations, crimps, and microcompressions are induced or diminished.
- Fibres break, resulting in changes in length distribution and a decrease in mean-fibre length. A small amount of fibre wall material also dissolves.

All these changes occur simultaneously and are primarily irreversible. The extent of the changes depends on the morphology of the fibres, 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 fibres within it receive the same treatment. The furnish (as it is now referred to) can also be treated with chemical additives. These include resins to improve the wet strength of the paper, dyes and pigments to affect the color of the sheet, fillers such as talc and clay to improve optical qualities, and sizing agents to control

Table 2.4 Common pulp stock additives

Acids and bases:
Control of pH
Sizing agents:
Water repellent
Dry strength additives:
Strength and stiffness (starch)
Wet strength additives:
Linking of fibers (polymers)
Fillers:
Gloss, brightness, and opacity (kaolin, TiO_2)
Defoamers:
Reduce foam and entrained air (surfactants)

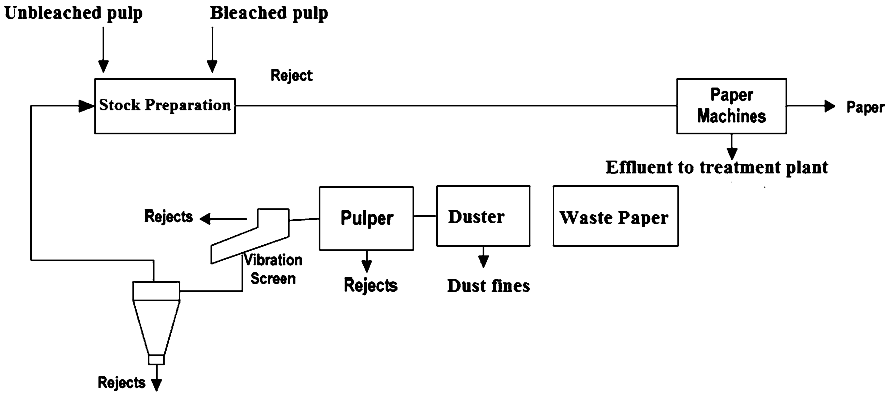

Fig. 2.2 A flow diagram for a typical papermaking process

penetration of liquids and to improve printing properties (Krogerus 2007; Bajpai 2004; Hodgson 1997; Davison 1992; Neimo 2000; Roberts 1996, 1997). The commonly used additives are shown in Table 2.4.

After stock preparation, the next step is to form the slurry into the desired type of paper at the paper machine. A flow diagram for a typical papermaking process is shown in Fig. 2.2. The actual papermaking process consists of two primary processes:

Wet end operation:

In wet end operations, the cleaned and bleached pulp is formed into wet paper sheets.

Dry end operations:

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 (Ishiguro 1987; Buck 2006; Atkins 2005; Lund 1999 and Malashenko and Karlsson 2000). Twin wire formers have become the state-of-the-art design (Malashenko and Karlsson 2000). In twin wire formers, the fibre 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 Fourdrinier 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 paper making machine is composed of three main sections: the forming section, the press section, and the dryer section. A paper slurry consisting of around 0.5–1.0 % fibre, 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 fibres to form a very wet, and weak paper. The paper is then pressed, heated, dried, resulting in a continuous roll or "web" which can be further finished as desired or required (Biermann 1996; Smook 1992). Figure 2.3 shows the details of the papermaking process; Fig. 2.4 shows Schematic of Fourdrinier paper machine. 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 1992). 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 cross currents, 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 eight-inch stock depth at a rate of 400 ft/min. If faster

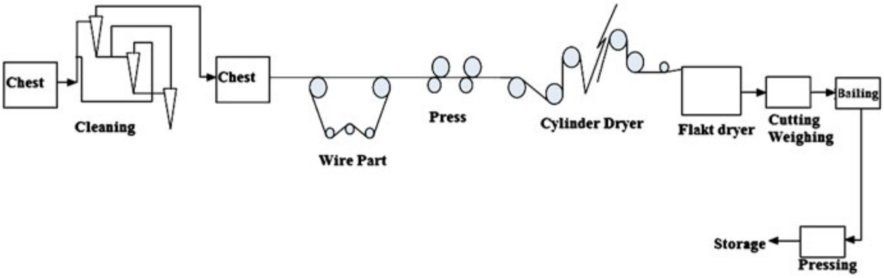

Fig. 2.3 Details of papermaking process

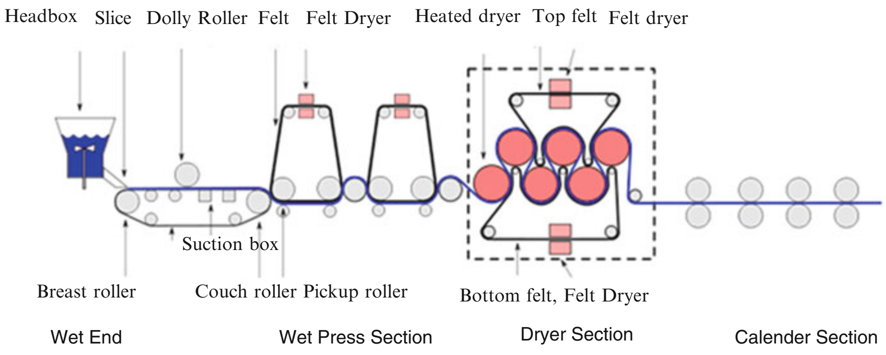

Fig. 2.4 Schematic of Fourdrinier paper machine

production speeds are required the stock must be fed under pressure. These machines can operate at speeds greater than 4,000 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 % fibres, with the make-up consisting of water. As the water is removed from the slurry, the fibres 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 mesh per inch, 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 per 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 fibres 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 fibres 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 fibres are still agitated from the effects of the headbox.

The first set of de-watering 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 on 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 increased 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 % fibre content. Above the first couple of suction boxes a skeleton roll covered with wire may ride on 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 elements-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 fibres are allowed to settle, and the paper appears light. If the watermark elements are below the dandy roll surface, more fibres 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 fibres 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. The First Twin Wire machines were constructed so that the headbox 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 de-watering 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 1992). Instead of pouring fibres through the forming wire, his machine dipped the forming wire into a vat, much in the same manner as hand made paper. This allowed him to create water marks 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 fibre 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.

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 allows 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 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 1996).

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 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 significantly affected 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.

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 1996). 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 neighbours 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 of the surface of each drier and is kept tight by means of stretch rolls. These felts also are 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 with-out 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 two pounds 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 which 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 eleven 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 by-pass the calender and go directly to the reel. Some paper machines use two calender stacks set so that the sheet passes 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.

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 the uniform surface. In the final stages the web is rewound and slit into two or more rolls and if needed sheeted.

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 either be performed on the paper machine or on a stand alone unit (Smook 1992; Latta 1997). 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 dryer section, is directed down into a vat and through another set of drying cans. Size presses are located after the between two dryer sections and applies 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 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, chemicals, improve adhesion characteristics, improve wear, or some other property. Coatings can be classified as aqueous, solvent, high solids, or extrusion, coatings. 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.

After the chemical processes have been completed, physical processes, like super calendering, cockling, and embossing, can be used to create the desired surface texture to the paper (Smook 1992). Super calendering uses friction and pressure to create a very smooth and glossy paper surface. The super calender 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 vat sizing the web then subjecting it to high velocity air dryers under high tension, 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 offline press, where it is subjected to an engraved cylinder. The concept is similar to the dandy roll, but since the paper fibres cannot be redistributed the surface of the paper is raised or depressed.

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 1996). 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 super calendering, 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 on-line 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, are 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″×11″, 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.

References

Adams TN (1992) Lime reburning. In: Kocurek MJ (ed) Pulp and paper manufacture, vol 5, 3rd edn. TAPPI/CPPA, Atlanta/Montreal, p 590

Annergren G, Lundqvist F (2008) Continuous kraft cooking: research and applications. STFI-Packforsk, Stockholm, 82 pp

Arpalahti O, Engdahl H, Jantti J, Kiiskila E, Liiri O, Pekkinen J, Puumalainen R, Sankala H, Vehmaan-Kreula J (2000) Chapter 14: White liquor preparation. In: Gullichsen J, Paulapuro H (eds) Papermaking science and technology, vol 6B. Fapet Oy, Helsinki, p 135

Arppe M (2001) Mechanical pulp: has it got a future or will it be discontinued? Int Papwirtsch 10:45–50

Atkins J (2005) The forming section: beyond the fourdrinier. Solutions! :28–30

Bajpai P (2004) Emerging technologies in sizing. PIRA International, Leatherhead, 159 pp

Bajpai P (2005) Technological developments in refining. PIRA International, Leatherhead, 140 pp

Bajpai P (2008) Chemical recovery in pulp and paper making. PIRA International, Leatherhead, 166 pp

Bajpai P (2012) Environmentally benign approaches for pulp bleaching, 2nd edn. Elsevier, Amsterdam

Bajpai P (2013) Recycling and deinking of recovered paper. Elsevier Science, Amsterdam

Baker C (2000) In: Baker C (ed) Refining technology. Pira International, Leatherhead, 197 pp

Baker CF (2005) Advances in the practicalities of refining. In: Scientific and technical advances in refining and mechanical pulping, 8th Pira International refining conference, Pira International, Barcelona, 28 February–March 2005

Biermann CJ (1996) Handbook of pulping and papermaking, 2nd edn. Academic, San Diego, p 754

Buck RJ (2006) Fourdrinier: principles and practices, 2006 In: TAPPI papermakers conference, Atlanta, 24–28 April 2006, Session 15, 13pp

Casey JP (1983a) Chemical pulping: a perspective. Tappi J 66(1):155–156

Casey JP (1983b) Mechanical and chemi-mechanical pulping: a perspective. Tappi J 66(6):95–96

Davison RW (1992) Internal sizing. In: Hagemeyer RW, Manson DW (eds) Pulp and paper manufacture, vol 6. TAPPI/CPPA, Atlanta/Montreal, p 39

EPA (2001a) Pulp and paper combustion sources national emission standards for hazardous air pollutants: a plain English description. U.S. Environmental Protection Agency. EPA-456/R-01-003. September 2001. http://www.epa.gov/ttn/atw/pulp/chapters1-6pdf.zip

EPA (2001b) Pulping and bleaching system NESHAP for the pulp and paper industry: a plain English description. U.S. Environmental Protection Agency. EPA-456/R-01-002. September 2001. http://www.epa.gov/ttn/atw/pulp/guidance.pdf

EPA (2002) Profile of the pulp and paper industry, 2nd edn. EPA Office of Compliance Sector Notebook Project. U.S. Environmental Protection Agency. EPA/310-R-02-002. November 2002

Farr JP, Smith WL, Steichen DS (1992) Bleaching agents (survey). In: Grayson M (ed) Kirk-Othmer encyclopedia of chemical technology, vol 4, 4th edn. Wiley, New York, p 271

Fredette MC (1996) Section 2, Chapter 2: Pulp bleaching: principles and practice. In: Dence CW, Reeve DW (eds) Bleaching chemicals: chlorine dioxide. Tappi Press, Atlanta, p 59

Gullichsen J (2000) Fibre line operations. In: Gullichsen J, Fogelholm CJ (eds) Chemical pulping – papermaking science and technology. Book 6A. Fapet Oy, Helsinki, p A19

Hodgson KT (1997) Overview of sizing. In: Tappi sizing short course, Session 1. TAPPI, Nashville (April 14–16, 1997)

Holik H (2006) Stock preparation. In: Sixta H (ed) Handbook of paper and board. WILEY-VCH, Weinheim, pp 150–206

Ince PJ (2004) Pulping – fibre resources. In: Burley J, Evans J, Youngquist JA (eds) Encyclopedia of forest sciences. Elsevier, Oxford, pp 877–883

Ishiguro K (1987) Paper machine. Jpn Tappi 41(10):44–50

Krogerus B (2007) Chapter 3: Papermaking additives. In: Alen R (ed) Papermaking chemistry: papermaking science and technology, vol 4, 2nd edn. Finnish Paper Engineers' Association, Helsinki, pp 54–121, 255 pp

Krotscheck AW (2006) In: Sixta H (ed) Handbook of pulp. WILEY-VCH, Weinheim, pp 512–605

Latta JL (1997) Surface sizing I: overview and chemistry. In: Tappi sizing short course, Session 5. TAPPI, Nashville (April 14–16, 1997)

Ljokkoi R (2000) Pulp screening applications. In: Gullichsen J, Fogelholm C-J (eds) Chemical pulping. Papermaking science and technology, vol 6A. Fapet Oy, Helsinki, pp A603–A616

Lumiainen J (2000) Chapter 4: Refining of chemical pulp. In: Papermaking science and technology, vol 8, Papermaking part 1: Stock preparation and wet end. Fapet Oy, Helsinki, p 86

Lund A (1999) The paper machine 200 years Nord. Pappershistorisk Tidskr 27(2):9–16

Malashenko A, Karlsson M, (2000) Twin wire forming – An overview. In: 86th annual meeting, Montreal, Que, Canada, 1–3 February. 2000, Preprints A, pp A189–A201

Malinen, Fuhrmann A (1995) Recent trends in bleaching of chemical pulp. Paperi ja puu 77(3):78–83

Marcoccia B, Prough JR, Engstrom J, Gullichsen J (2000) Chapter 6: Continuous cooking applications. In: Gullichsen J, Fogelholm C-J (eds) Papermaking science and technology, vol 6A, Chemical pulping., pp A512–A570

McDonough T (1992) Bleaching agents (pulp and paper). In: Grayson M (ed) Kirk-Othmer encyclopedia of chemical technology, vol 4. Wiley, New York, p 301

McDonough TJ (1995) Recent advances in bleached chemical pulp manufacturing technology. Part 1: extended delignification, oxygen delignification, enzyme applications, and ECF and TCF bleaching. Tappi J 78(3):55–62

Neimo L (2000) Internal sizing of paper. In: Neimo L (ed) Papermaking chemistry. Tappi Press/Fapet Oy, Atlanta/Helsinki, p 150

Paulapuro H (2000) Stock and water systems of the paper machine. In: Gullichsen J, Fogelholm C-J (eds) Papermaking science and technology, vol 8, Papermaking part 1, Stock preparation and wet end. Fapet Oy, Helsinki, p 125

Rapson WH, Strumila GB (1979) The bleaching of pulp. In: Singh RP (ed) Chlorine dioxide bleaching, 3rd edn. Tappi Press, Atlanta, p 113

Reeve DW (1989) Bleaching chemicals. In: Kocurek MJ (ed) Pulp and paper manufacture, vol 5, Alkaline pulping. TAPPI/CPPA, Atlanta/Montreal, p 425

Reeve DW (1996a) Section 1, Chapter 1: Introduction to the principles and practice of pulp bleaching. In: Dence CW, Reeve DW (eds) Pulp bleaching: principles and practice. Tappi Press, Atlanta, p 1

Reeve DW (1996b) Section 4, Chapter 8: Pulp bleaching: principles and practice. In: Dence CW, Reeve DW (eds) Chlorine dioxide in bleaching stages. Tappi Press, Atlanta, p 379

Reeve DW (2002) The kraft recovery cycle, Tappi kraft recovery operations short course. Tappi Press, Atlanta

Ressel JB (2006) In: Sixta H (ed) Handbook of pulp. WILEY-VCH, Weinheim, pp 69–105

Roberts JC (1996) Neutral and alkaline sizing. In: Roberts JC (ed) Paper chemistry, 2nd edn. Chapman and Hall, London, p 140

Roberts JC (1997) A Review of Advances in Internal Sizing of Paper. In: Baker CF (ed) The fundamentals of paper making materials: transactions, 11th fundamental research symposium (Cambridge), vol 1. PIRA International, Leatherhead, p 209

Sixta H (2006) In: Sixta H (ed) Handbook of pulp. WILEY-VCH, Weinheim, pp 2–19

Smook GA (1992) Handbook for pulp and paper technologists. Angus Wilde Publications, Inc, Vancouver, 425p

Stevens WV (1992) Refining. In: Kocurek MJ (ed) Pulp and paper manufacture, vol 6, 3rd edn. TAPPI/CPPA, Atlanta, p 187

Tran H (2007) Advances in the kraft chemical recovery process, Source 3rd ICEP international colloquium on eucalyptus pulp, 4–7 March, Belo Horizonte, Brazil, 7pp

USEPA (1998) Pulp and paper NESHAP: a plain English description www.epa.gov/ttnatw01/pulp/guidance.pdf

Vakkilainen EK (2000) Chapter 1: Chemical recovery. In: Gullichsen J, Paulapuro H (eds) Papermaking science and technology, vol 6B. Fapet Oy, Helsinki, p 7

Venkatesh V (1992) Chapter 8: Lime reburning. In: Greenand RP, Hough G (eds) Chemical recovery in the alkaline pulping process, vol 6B. Tappi Press, Atlanta, p 153

Chapter 3
Environmental Consequences of Pulp and Paper Manufacture

Abstract Pulp and paper companies have faced environmental issues for many years because of the resource-intensive nature of their industry. The pulp and paper mills represent a major source of polluting materials which are very different regarding their characteristics and quantities. 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. The environmental consequences of pulp and paper manufacture are presented in this chapter. A special attention is focused on the pulp bleaching as the most pollution process of the chemical pulp manufacturing.

Keywords Kraft pulping • Pulp bleaching • Environment • Wastewaters • Air emissions • Liquid • Discharges • Solid wastes

The pulp and paper industry has been considered a major consumer of natural resources, energy and water and is a significant contributor of pollutant discharges and emissions to the environment. It ranks fourth among industrial sectors in emissions of Toxics Release Inventory (TRI) chemicals to water, and third in such releases to air. Technological changes, the use of environmental and energy management systems, investments in environmental measures and continuous improvements, the increased recycling of paper, the employment of highly trained and committed personnel have allowed for a stepwise reduction in the environmental footprint, and have reduced emissions by 80–90 % or more on a product-specific basis (per tonne of product) since about 1980. In the United States, the paper industry is the largest user of industrial process water (per tonne of product) (US EPA 2002) and the third largest industrial consumer of energy (US DOE) (Papercutz: PlanetArk 2008).

Paper's impact on the environment continues even after it has been thrown away. As at early 2008 in the United States, paper and paperboard accounted for the largest portion (34 %) of the municipal waste stream, and 25 % of discards after recovery of materials for recycling and composting. The problem with all this paper being

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thrown away is not just about landfill space. Once in a landfill, paper has the potential to decompose and produce methane which is, a greenhouse gas (GHG). It has 21 times the heat-trapping power of carbon dioxide. Finally, transportation throughout the system also has considerable environmental impacts. Harvested trees or recovered paper are transported to pulp mills, rolls of paper are transported to converters, and finished paper products are transported to wholesale distributors and then on to their retail point of sale. Transportation at each of these stages consumes energy and results in emission of GHGs.

There is a strong drive to improve the impact of the pulp and paper industry upon the environment. This includes moves to sustainable forest management with Forestry Stewardship Certification and removal of harmful bleaching technologies. Impacts on the environment can potentially come from toxic and hazardous chemicals in water and air emissions, odor-causing chemicals, thermal loading to natural waterways, air pollutants from combustion, and solid wastes. The industry is taking steps to reduce environmental impacts by increasing the use of recycled paper, improving energy efficiency, and making capital investments for effective compliance with regulations.

A pulp mill influences the water and air near the mill, and the emissions are followed by measurements and there are emission limits set by authorities. Disposal of solid waste, recycling of fibres and use of land and forest are gaining attention. Other effects of a pulp mill on the nearby society are smell, noise and influence of traffic related to the transport of raw materials and products. Table 3.1 shows parameters important to demonstrating continuous improvements towards a minimum impact mill.

The environmental impacts of kraft pulp production mainly result from the chemicals used for both cooking and bleaching. Some of which are: sulphur, chlorine, chlorinated compounds, remaining organic and inorganic materials, lignin and undissolved fibre material, typically mixed up in the black liquor, and eventually sodium and magnesium salts, chelating agents and heavy metals such as manganese or iron. Thus, the main environmental problems of kraft pulp production are water consumption, wastewater loads and gaseous emissions, including malodorous sulfur compounds and carbon dioxide (European Commission 2001, 2013).

The most significant environmental impacts of the pulp and paper manufacture result from the pulping and bleaching processes. Some pollutants are released to the air, others are discharged to the wastewaters, and solid wastes are also generated (Bajpai 2001). Much research has focused upon 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, non biodegradable and have the tendency 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 and Bajpai 1996; Bajpai 2001).

The impact of pulp effluent has been studied in some detail in Scandinavia, where significant efforts have been made to reduce pulp mill discharges. A three-

Table 3.1 Important parameters followed in order to demonstrate improvements towards a minimum impact mill

Water	Air	Solid Waste	Other
Water usage	Particulates	Solid waste generated	Accidental releases
Bleach plant effluent	Total reduced sulfur	Solid waste disposal	Accidental releases
			Non-compliant events
Final effluent	Methanol	Landfill	SARA 313 releases
BOD	Chloroform	Recycled	Energy use/energy export
COD	Chlorine	Energy	Transportation effects aesthetics
Suspended solids	Chlorine dioxide	Hazardous waste	Site appearance
AOX			
Dioxins and furans	CO/CO_2	Elimination	Odor
Color	NOX		Noise
Biological tests	SO_2		
Nutrients	VOC		
Heavy metals	Dioxins and furans		
Safety	Opacity		
	Hazardous air pollutants		

year study of pulp mill effluents in the Baltic Sea showed that near the effluent outflow fish biomass was low, and species composition had changed with perch (Perca fluviatilis) showing reduced reproduction, changes in physiology and damage to the spinal column. Presence of a pulp mills affected recruitment to fish populations over an area of several square kilometres, thus having an economic impact on fisheries. In the case of perch reproductive losses of 30–70 % were made in the affected area. The effluent also affected the diversity, biomass and distribution of invertebrates and plants, including the crustacean Pontoreia affinis and the bivalve mollusc Macoma baltica (Södergren 1989). Further research revealed that the distribution of the seaweed bladder wrack (Fucus vesiculosus) was affected by pulp mill effluent, with the algae disappearing from the most polluted areas. Pollution also decreased the numbers of mussels and increased the frequency of malformed larvae. Bleached pulp mill effluents also apparently increased the prevalence of three fish diseases (Södergren 1993):

- Fin erosion in perch and goldfish (Carassius auratus studied in New Zealand),
- Jaw deformity in pike
- Gill cover deformity in perch

A series of studies in Scandinavia found that chronic effects of pulp mill effluents could include:

- Changes in reproductive and life cycles, deformities in embryos, stunted growth and higher egg mortalities;

- Deformities in bones and gill erosion in fish;
- Biochemical and physiological disturbances, including reduced ability of muscles to store carbohydrates, impaired stamina and increased susceptibility to predation and disease;
- Changes in habitat and community structure (Abel 1993).

Inspite of that, the relationships between specific effluent compounds and toxic effects is poorly understood, and sublethal biological effects occur even when dilution of waste is quite high. Synergistic and/or antagonistic effects amongst chemical compounds are probably important in some cases (Priha 1991). Toxicity is affected by the type of wood used and the procedures used for processing (Fandry et al. 1989). Research funded by the Department of Fisheries and Oceans, Canada, and the Ontario Ministry of Environment Research Advisory Council found that several species of fish exhibited damage from pulp mill effluents at Jackfish Bay, Lake Superior. The white sucker (Catostomus commersoni) showed a variety of responses listed below when exposed to kraft pulp mill effluent:

- Reduction in body size
- Delayed sexual maturity
- Smaller gonads
- Increased liver size

Similar effects were observed in lake whitefish (Coregonus clupeaformis) and longnose sucker (Catostomus catostomus). The mill discharge into Jackfish Bay was reduced by installation of an aerated stabilisation basin in 1989. Studies in 1993 showed no evidence of recovery in reproductive function, but did find limited improvement in liver size. Further research on white sucker fish found that loss of reproductive capability occurred near pulp mills with and without chlorine bleaching, and at sites with secondary effluent treatment (Munkittrick and van der Kraak 1994). Researchers now believe that some effects on fish are caused by non-chlorinated compounds, probably coming from the wood itself. One of these compounds has been positively identified as a steroid (Cockram and Richard 1994). Dioxins were found in the effluent of two thirds of Japanese pulp and paper mills. In October 1990, research by Ehime University revealed that fish caught in sea water near pulp mills in lyo-Mishima contained 9.4 parts per thousand of dioxin. The Ministry of International Trade and Industry called for the 32 mills producing bleached kraft pulp by chlorine gas to change to oxygen or chlorine dioxide. There are now no mills in Japan using chlorine gas bleaching (Kondo 1993). Other by-products of the process include 'non-filterable material' consisting of bark and wood fibres. These materials can also be of threat to aquatic organisms forming fibre mats on ocean bottoms, eliminating or altering bottom-dwelling organisms (IIED 1994). Toxic effects can extend to other groups of animals as well. In North America, both peregrine falcon. and blue herons have suffered reproductive failure through accumulation of organochlorines from pulp mill effluent.

There is a development to close up water circuits in pulp and paper mills and a further reduction of discharges can be expected (towards effluent free mills).

However, today there are no kraft mills operating full time, which completely recover all bleach plant effluent. Few CTMP mills, sodium-based sulphite pulp mills and a few producers of corrugating medium and testliner using recycled fibre have realised zero effluents to water.

There is a debate about minimum-impact pulp manufacturing in the recent past (Axegard et al. 1997; Hanninen 1996; Elo 1995). This minimum-impact mill stands for a concept with a broader range of issues and challenges covering minimisation of resource consumption and emissions, minimising crossmedia effects, taking into account economic aspects and working environment.

The pulp mills caused serious emissions of sulphur in the past but in the recent years especially the sulphur air emissions has been reduced significantly which could be attributed to advancement of process technology. In most of the countries, the recycling of fibres 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 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 fibres 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 focussed 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 lead 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), total suspended solids (TSS) etc. 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 viz. 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 been largely 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 has 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 as 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 unchlorinated toxic organic compounds into receiving waters, was the installation of external treatment plants of different designs (Bajpai and Bajpai 1996).

There has been a development to close up water circuits in pulp and paper mills (McDonough 1995; Chirat and Lachenal 1997; Pryke 2003; Bajpai and Bajpai 1999; Bajpai 2012). And in regions with scarce water resources or dry climate, further reduction of water use per tonne of product will be essential in order to keep the capital-intensive production sites. Those sites will probably be the first movers that develop new techniques and management methods toward water-saving solutions. Other driving forces for developing less water using techniques will probably be the regional costs of raw and waste water. However, there is a trend not to push too much further the closure of water circuits in normal pulp and paper mills because of the often involved technical drawbacks such as scaling, increased corrosion, accumulation of salts or non-process elements in process waters, etc. Today there are no kraft mills operating full time, which completely recover all bleach plant effluent. One CTMP mill, a sodium-based bleach plant of a sulphite pulp mill and a few producers of corrugating media and Testliner using recycled fibre have realised zero effluents to water (European Commission 2013). Under an integrated perspective, the aim is to move towards the minimum impact pulp and paper manufacturing. In a few paper mills, an increased reuse of treated process waters by implementing production-integrated advanced waste water treatment systems can be observed. However, water use is not to be seen separately from the other main elements for production which are energy, fibres and chemical additives and proper functioning of all technical devices. Energy consumption, use of chemical additives, runnability of the paper machines and product quality are closely linked to the water used per tonne of pulp or paper and should be assessed in an integrated way.

In paper mills an increased reuse of treated process waters by 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 also future priorities of environmental actions in pulp and paper industry.

3.1 Water Pollution

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 3.2. Pollutants such as chlorinated phenolics and dioxins are toxic, non biodegradable and have the tendency to contaminate food chains through bioaccumulation. The dioxins are known for their extreme toxicity and are believed to be carcinogenic (Bajpai 2001). Table 3.3 shows the list of 12 polychlorinated phenolics selected by EPA for regulation.

The most common chlorinated phenolics in bleached kraft pulp mill effluents are tri- and tetra chloroguaiacols (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 alone was used in the bleaching stage. When a 70:30 chlorine dioxide:chlorine ratio was used in the first stage, the catechol and guaiacol portion decreased to 46 %, and at 100 % chlorine dioxide substitution, only

Table 3.2 Chlorinated organic compounds in bleach plant effluents

Types of chlorinated compounds	Variations (numbers)
Acids, esters, aldehydes, furans, pyrenes	77
Phenols and phenol ethers	52
Aldehydes and ketones	66
Hydrocarbons	75
Alcohols	25
Dioxins and furans	20
Miscellaneous	15
Total	330

Based on McKague and Carlberg (1996)

Table 3.3 Regulated chlorophenols

2,3,4,6-Tetrachlorophenol
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
Pentachlorophenol
3,4,5-Trichloroguaiacol
3,4,6-Trichloroguaiacol
4,5,6-Trichloroguaiacol
3,4,5-Trichlosyringal
3,4,5,6, Tetrachlorocatechol
3,4,6-Trichlorocatechol
3,4,5-Tetrachlorocatechol
3,4,5,6-Tetrachloroguaiacol

Based on Vice and Carrol (1998)

10 % of the chlorinated phenolics were of the catechol and guaiacol type (Liebergott et al. 1989).

Bleach kraft mill effluent is a complex mixture of chlorinated and non-chlorinated products of lignin and/or extractives of wood that imparts dark colour to the effluent. Coloured effluent may result in the following adverse effects upon the receiving water body:

(a) Colour reduces the visual appeal and recreational value of the water.
(b) Colour, derived from lignin, is an indicator of the presence of potentially inhibiting compounds.
(c) Colour affects downstream municipal and industrial water uses, and increases the cost and difficulty of pre-treatment for industrial processes.
(d) Colour retards sunlight transmission, thus reducing the productivity of the aquatic community by interfering with photosynthesis.
(e) Colour-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.
(f) Colour bodies exert long term BOD (20–100 days) that cannot be measured in terms of 5-day BOD.

Bleached kraft mill effluent can effect 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 (Sundelin 1988; Sodergren et al. 1993). Bleached kraft and bleached sulphite 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 a tendency to bioaccumulate. Low molecular weight chlorinated organic compounds significantly affect the biology of aquatic ecosystems.

A major part of the organically bound chlorine (80 %) is believed to be heterogeneous material of relatively high molecular weight compounds. These compounds apparently contribute little to the effluent BOD and acute toxicity. Their major contribution is towards colour, 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 bio-accumulate in fish and mussels (Suntio et al. 1988).

Chlorinated dioxins, which are present in very low concentrations in the bleach plant effluent (usually in ppt 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 bio-accumulable. The structures of the most toxic forms of dioxin and furan molecules are shown in Fig. 3.1. A dioxin molecule is bonded by two oxygen atoms and a furan molecule by a single oxygen atom and a direct bond (Rappe and Wagman 1995). Under standard atmospheric conditions, all dioxins are solid and are characterised by low vapour pressure and limited solubility in water. Polychlorinated dioxins toxicity depends on the location and the number of additional chlorine atoms attached to the benzene rings. PCDD/F 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 source of dioxins in the pulp and paper industry is the bleaching process in which chlorine is used as reagent. It was found that pulp chlorination stage is the first point where dioxins are generated (McKague and Carlberg 1996). The chlorinated pulp contains largest concentration of dioxins that are solubilized in the next alkaline extraction stage. The quantity of dioxins in the bleaching effluents is very 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 Environmental Protection Agency (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).

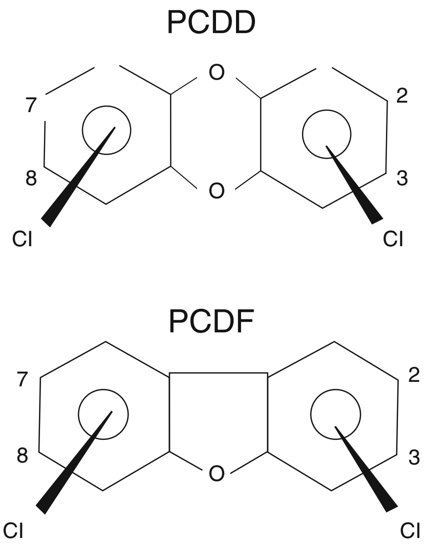

Fig. 3.1 Polychlorinated dibenzodioxins (*PCDD*) and polychlorinated dibenzofurans (*PCDF*)

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 standardised techniques. Moreover, many studies continue to suggest that even the most advanced ECF mills produce effluent with a higher toxicity than TCF mills (Vidal et al. 1997; Cates et al 1995; Kovacs et al. 1995; Rappe and Wagman 1995; Rosenberg et al. 1994). 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 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 % chlorine dioxide 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. One group of chemicals which has given rise to concerns are the chelating agents (Ethylenediaminetetraacetic acid (EDTA), diethylene triamine 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 sulphate 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 to 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 mobilise 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 which 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 requires 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 build up of non-process elements, particularly in the bleach lines. The purging of non-process 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 Atmospheric Pollution

Although atmospheric pollution is generally reckoned to be less important than discharges to water it remains important in some areas. Sulphur dioxide is the most important component of acid rain on a global basis, and chlorinated solvents released by chemical pulping contribute to both global warming and the breakdown of the ozone layer. Hydrogen sulphide, chloroform and carbon tetrachloride can all be released from mills and result in significant health risks to workers and nearby residents. The US Environmental Protection Agency has recently added the pulp and paper industry to its category of "major sources of hazardous air pollutants" due to the presence of chlorine, other volatile organic compounds and chloroform in waste gases. In addition, sulphuric acid fumes, released from some pulp factories, can damage the bronchial tract. In Russia, the area round Bratsk in the east Siberian taiga, was declared a disaster area in 1992, as a result of air pollution from the local pulp and board producer.

The US Environmental Protection Agency estimates that people regularly eating fish caught near pulp mills have 1,000 times the chance of developing certain cancers. In 1989, a study by the Canadian Department of Health and Welfare reported that residents of British Columbia had the highest average levels of dioxin in body tissue in the country. Several areas of British Columbia, have subsequently banned shellfish collection due to mill pollution (Greenpeace 1990). Although the impacts of dioxins remain controversial, some are now regarded as carcinogens by most regulatory authorities. Dioxin pollution problems have been addressed by many pulp mills, other effects, less clearly understood, have been identified in fish populations near pulp mills in Scandinavia and Canada (Carey et al. 1993). Workers at pulp and paper mills appear to face some direct and long term risks from pollution. A study by the International Labour Office found wide differences in accident rates between countries and some industry-specific diseases occurred. In Finland, a number of cancers were recorded at high incidence levels amongst workers in pulp mills, probably as a result of chemicals used in the pulp process and biological agents (International Labour Organisation 1992). Concern about dioxins has extended beyond the pulp-making process to the risks from residues remaining in paper and sanitary products, particularly in Europe where scares about the impact of dioxins in coffee filters, disposable nappies and tampons has been the subject of much consumer concern. In Sweden, regulations have been tightened as a result of findings about dioxins in paper waste effluent and alternative oxygen bleaching processes have been encouraged, so that by 1993 TCF paper was available (Women's Environmental Network 1989). In North America, where anxiety about chlorine residues has not been as high, the industry has chosen to use chlorine dioxide as the primary bleaching agent, resulting in discharge which is elemental chlorine free. These developments are not without their own controversy, and questions remain about the pollution from TCF plants. Some campaign groups, including notably Greenpeace, remain totally opposed to use of chlorine in any form. In a further development, several plant in North America and Scandinavia are now attempting to develop completely closed loop systems, where there would be zero discharge of any effluent.

In the past, chemical pulp mills have caused serious emissions of sulphur (acidification) but in recent years, sulphur air emissions have especially been reduced by substantial progress in process technology. Recovery boilers and lime kilns are still important sources of air pollutants such as particulate matter, NOX, SO_2, CO and H_2S in some cases. Because of the need for heat and power, most pulp and paper mills operate on-site power plants, auxiliary boilers, steam blocs or combined heat and power plants. These plants contribute significantly to total industrial emissions-despite high efficiency combustion and efficient flue gas cleaning. The key air emissions connected to the combustion of fuels for energy production (NOX, SO_2, dust) will thus remain an issue for the sector as Directive 2001/81/EC of the European Parliament and of the Council on national emission ceilings for certain atmospheric pollutants (NEC Directive) aims at limiting emissions of acidifying and eutrophying pollutants and ozone precursors. The objective to move towards the long-term objectives of not exceeding critical levels and loads and of effective protection of all people against recognised health risks from air pollution will also demand some additional efforts from a number of mills that still have potential for improvement.

Air emissions from chemical pulp mills are primarily made up of particulates, hydrogen sulphide, oxides of sulphur and oxides of nitrogen. Micro-pollutants include chloroform, dioxins and furans, other organochlorines and other volatile organics. As with liquid effluent discharges, the levels of emissions are highly dependent upon the type of process technology employed and individual mill practice. Another important factor is the fuel type and quality. Whilst older mills caused severe air pollution, mitigating technology now exists to eliminate most harmful gas and particulate emissions. Whether this technology is utilised 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 (GHGs) 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 some 450 million carbon dioxide equivalent units per year.

While the advantages of in-mill process changes with respect to the use of water resources and concomitant impacts upon receiving aquatic systems are well documented, the implications for 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 NOx 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 NOx emissions to 1 kg/tonne 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 suggest that overall releases of NOx, total reduced sulphur (TRS), sulphur dioxide and particulate matter are similar for both production processes (Södra Cell 1996). While NOx, carbon dioxide, TRS/sulphur dioxide and particulate matter continue to be important, there are other emissions which 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 area of concern (Environment Canada 1998). PCBs, 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 released 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, or trace air contaminants and total reduced sulphur 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 sulphur (Södra Cell 1996). Both of these systems were added at the Värö Bruk mill. This mill already used 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 sulphur emissions. Accordingly, upgrading of mills to closed loop operation should ideally include installation of non-direct contact, low odour 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 sulphur dioxide (McCubbin 1996).

Methanol and a wide range of other hazardous air pollutants and volatile organic compounds 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 hazardous air pollutants (HAPs) and volatile organic carbon (VOC) compounds 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 (USEPA 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 volatilise from the treatment ponds of these mills, but were almost non-existent 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 (Juuti et al. 1996; Calamari et al. 1994). 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 recognised the major benefit that TCF systems are not expected to produce HAPs in the bleach plant (USEPA 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 upon 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.

3.3 Sludge and Solid Waste

Different types of sludge and solid wastes are generated in the Pulp and Paper Industry at different production processes. Treatment of wastewater generated at pulping, papermaking, and deinking processes is the main source of wastewater treatment sludge and deinking sludge (Monte et al. 2009; Gavrilescu 2004, 2005; Abubakr et al. 1995). Table 3.4 shows solid waste generated in Pulp and Paper mills. Table 3.5 shows generation of Waste in a Kraft mill (Gavrilescu 2004).

About 300 kg of sludge is produced for each one ton of recycled paper (Balwaik and Raut 2011). The amount of waste generated in paper production varies greatly within different regions, because of different recycling rates. In Finland, the ratio of recycled fibre production to paper production can be expected to be smaller than example in central Europe (Kujala 2012). This is due to the reason that most of the paper produced in Finland is exported to other countries and so the amount of recovered paper is relatively low. According to WRAP (2010), over 5 million tons of paper and board was produced in 2007. At the same time, the production of paper mill sludge from Recycled fibre production was approximately 1 million tons (Rothwell and Éclair-Heath 2007).

The generation of wastewater treatment sludge vary widely among mills (Monte et al. 2009; Abubakr et al. 1995). Not much data is available on total waste generation. This is due to the fact that most of the pulp and paper mills already have processes applied to internally treat the wastes which reduce the generation of solid

Table 3.4 Solid waste generated in pulp and paper mills

Pulp mill	Paper mill
Rejects	Rejects
Green liquor sludge, dregs and lime mud	Deinking sludge
Wastewater treatment sludge	Primary sludge
Chemical flocculation sludge	Secondary sludge or biological sludge

Table 3.5 Generation of waste in a kraft mill

Waste
Wood wastes:
Sawdust coming from the slasher deck
Bark falling from the debarking drum
Pins and fines from chip screening
Wood waste from woodyard
Knots from pulp deknotting
Sodium salts from recovery boiler
Dregs from causticizing
Grit from causticizing

Based on Gavrilescu (2004)

waste. This applies to bark residues from debarking which are incinerated in the bark boiler and, as a result, only ashes remain as waste. The same can apply to sludge incineration. The amount of waste generated when virgin fibres are used as raw material depends mainly on the pulping process used. European Commission (2001) reports that in Europe, 65 % of total pulp production is kraft pulp which produces about 100 kg/Adt of wastes. Semi-chemical and mechanical processes produce about 60 kg/Adt.

CEPI (2006) has reported that in 2005, the total production of paper in Europe was 99.3 million tonnes. This generated 11 million tonnes of waste, representing about 11 % in relation to the total paper production. The production of recycled paper, during the same period, was 47.3 million tonnes generating 7.7 million tonnes of solid waste (about 70 % of total generated waste in papermaking) which represents 16 % of the total production from this raw material.

The amount of waste sludges generated from a mill using secondary fibre differ from a mill using virgin materials. Also, the composition is different. A greater amount of rejects is produced when processing recycled fibre, because of the unrecyclable filler proportion in the raw material. This problem is especially conspicuous in mills producing recycled paper from office waste, using highly filled grades as the raw material. Deinking mill sludge generally has a higher ash content; the kraft pulp mill sludge is found to be high on sulfur. Obviously, great variations occur within both plant types, depending on the processes and raw materials (Glenn 1997). The amount of wastes produced in paper mills based on recycled fibre depends mainly on the quality of recovered paper used as raw material. It also depends on the effort and expenses made in preparation of secondary fibres for certain product and process requirements.

Disposal of solid waste 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 (Ritchlin and Johnston 1998). However, the need to control the nonprocess elements will require purge points to prevent upsets in bleaching and recovery chemistry, and reduce corrosion of mill equipment (Gleadow et al. 1997a, b). 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 since, 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 un-recyclable wastes. 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 re-using 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 programmes.

Sludge from bleach 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 of these parameters continue to be important, improvements to secondary treatment and the move towards 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 (Martin et al. 1995; Fitzsimons et al. 1990; O'Connor and Voss 1992; Brezny et al. 1993; Kookana and Rogers 1995). 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 emphasised by the New Hampshire Department of Environmental Services following experiences in New Hampshire, United States. This body consider that the inherent variability in sludge composition necessitates extensive testing and monitoring prior to spreading on land. This followed the discovery of VOCs during post application testing in landfill groundwater where short paper fibre sludge had been used for remediation purposes. The potential for this problem was not identified through pre application 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 sulphur chemicals from the chlorine dioxide generator (Paleologou et al. 1997) due to the fact that sulphate compounds are by-products of chlorine dioxide generator and often used as make-up chemicals in bleaching and pulping. Increased chlorine dioxide production for ECF, and increased filtrate recycling heighten concentration of sulphur chemicals in process circuits. Because increased sulphur becomes a concern for non-process element control in closed loop designs, this increase necessitates disposal of excess sulphates. These eventually end up in effluent treatment in many current mills. Under anaerobic conditions, certain bacteria can reduce sulphate, 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 fibre sludge disposal will progressively diminish in importance. The impacts of burning this material must be continuously evaluated, and opportunities for more beneficial re-use 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). On an 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 fibre and spent liquors going to aquatic or land-based discharge. Processes that allow for a maximum of non-polluting and worker-safe re-use of pulping and bleaching by-products are needed.

Many companies choose to implement integrated waste management plans that seek to minimise residues to be sent to landfill and to further increase the share of residues that are reused, recycled or recovered (including energy recovery). The goals for the management of residues in the pulp and paper sector include their use as renewable fuels, as soil improvers or as raw materials for other industries or their conversion into added value products for other users. New concepts in the sector aim at a best possible usage and energetic recovery of most residues generated on-site, if possible recycling also the ashes, example in the construction or cement industry or using ash for soil stabilisation. The general target is minimising the amount of waste to be sent to landfills. These solutions aim to achieve waste reduction, resource recovery and energy efficiency at reasonable costs. Locally odour and noise nuisances from pulp or paper mills are expected to remain future priorities for environmental actions in the pulp and paper industry.

References

Abel, K (1993) Pulp mill effluents national pulp mills research program, CSIRO, Dickson

Abubakr S, Smith A, Scott G (1995) Sludge characteristics and disposal alternatives for the pulp and paper industry. In: Proceedings of the 1995 international environmental conference, Atlanta, GA, Tappi Press, 7–10 May 1995, pp 269–279

Aitken M (1995) Effects on soil fertility from applying paper mill sludge to agricultural land. Soil Use Manag 11:152–153

Andrews RS, Paisley MA, Smith M, Young RJ (1996) Formation and release of methanol and hydrogen chloride from DCE recovery boiler systems. Tappi J 79(8):55–160

Anonymous (1994) EPA report thrusts dioxins back into the spot light. ENDS Ref. No. 236, pp 21–24

Axegard P, Carey J, Folke J, Gleadow P, Gullichsen J, Pryke DC, Reeve DW, Swan B, Uloth V (1997) Minimum-impact mills: issues and challenges. In: Proceedings of the minimum effluent mills Symposium. Tappi Press, Atlanta, pp 529–541

Bajpai P (2001) Microbial degradation of pollutants in pulp mill effluents in advances in applied microbiology, vol 48. Neidleman S, Laskin A (eds), Academic, New York, pp 79–134

Bajpai P (2012) Environmentally benign approaches for pulp bleaching, 2nd edn. Elsevier, Amsterdam

Bajpai P, Bajpai PK (1996) Organochlorine compounds in bleach plant effluents – genesis and control. PIRA International, Leatherhead

Bajpai P, Bajpai PK (1999) Recycling of process water for closed mill systems. PIRA International, Leatherhead

Balwaik SA, Raut SP (2011) Utilization of waste paper pulp by partial replacement of cement in concrete. Int J Eng Res Appl 1(2):300–309. Available at: http://ijera.com/pages/v1no2.html

Bard S (1998) A biological index to predict pulp mill pollution levels. Water Environ Res 70(11):108–122

Bouchard J, Nugent HM, Berry RM (1995) A comparison between acid treatment and chelation prior to hydrogen peroxide bleaching of kraft pulps. J Pulp Pap Sci 21(6):203–208

Brezny R, Joyce T, González B, Slimak M (1993) Biotransformations and toxicity changes of chlorolignins in soil. Environ Sci Tech 27:1880–1884

Calamari D, Tremolada P, Guardo AD (1994) Chlorinated hydrocarbons in pine needles in Europe: fingerprint for the past and recent use. Environ Sci Tech 28:429–434

Carey JH, Hodson PV, Munkittrick KR, Servos MR (1993) Recent Canadian studies on the physiological effects of pulp effluent on fish. Environment Canada, Ottawa

Caron JR and Delaney G (1998) Initial learning from the BFR demonstrations. In: 84th annual meeting, technical section Canadian pulp & paper association. 27–30 January 1998, Preprints A, pp A379–A384

Cates DH, Eggert C, Yang JL, Eriksson K-E L (1995) Comparison of effluents from TCF and ECF. TAPPI J 78(12):93–98

Chirat C, Lachenal D (1997) Pulp producers race to keep up with technology. Pulp Pap Int 39(10):29–32

Cockram, Richard (1994) Are they doing their best for the environment? Eur Papermak 2(3), April 1994, Sweden

Confederation of European Paper Industry (2006) Special recycling 2005 statistics, (http://www.cepi.org)

Crawford RJ, Rovell-Rixx DC, Jett SW, Jain AK, Dillard DS (1995) Emissions of volatile organic compounds and hazardous air pollutants from oxygen delignification systems. In: 1995 international environmental conference, Atlanta, 7–10 May, Book 1, pp 575–587

Duncan A, Thia BC, Jelbart J, Donlon PJ (1995) Factors influencing the treatment of Australian pulp mill effluent. Appita J 48(4):295–298

Easton MDL, Kruzynski GM, Solar II, Dye HM (1997) Genetic toxicity of pulp mill effluent on Juvenile Chinook Salmon (Onchorhynchus Tshawytscha) using flow cytometry. Water Sci Technol 35(2):347–355

Elo A (1995) Minimum impact mill. In: Third global conference on paper and the environment, London, 26–28 March 1995, pp 105–110

Environment Canada (1998) Dioxins and furans and hexachlorobenzene inventory. environment Canada and the federal/provincial task force on dioxins and furans for the federal-provincial advisory committee for the Canadian environmental protection act draft 4. April, 1998

European Commission (2001) Reference document on best available techniques in the pulp and paper industry, Institute for prospective technological studies. Integrated Pollution Prevention and Control (IPPC), Seville

European commission (2013) Best Available Techniques (BAT) Reference document for the production of pulp, paper and board. Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control). Joint Research Centre, Institute for Prospective Technological Studies Sustainable Production and Consumption Unit European IPPC Bureau

Fandry, CB, Johannes RE, Nelson PJ (1989) Pulp mills: modern technology and environmental protection: report to Senator the Hon. John Button, Minister for Industry, Technology and Commerce, Commonwealth of Australia, Commonwealth Scientific and Industrial Research Organisation, June 1989

Fitzsimons R, Ek M, EL Eriksson K (1990) Anaerobic dechlorination/degradation of chlorinated organic compounds of different molecular masses in bleach plant effluents. Environ Sci Tech 24(11):1744–1748

Gavrilescu D (2004) Solid waste generation in kraft pulp mills. Environ Eng Manag J 3:399–404

Gavrilescu D (2005) Sources of solid wastes in pulp mills. Bull Polytechnic Inst Iasi (Buletinul Institutului Politehnic din Iasi) LI(LV):99–105

Germgard U, Teder A, Tormund D (1981) Chlorate formation during chlorine dioxide bleaching of softwood kraft pulp. Paperi Ja Puu 63(3):127–133

Gevert BS, Lohmander SF (1997) Influence of sulfur compounds, manganese, and magnesium of oxygen bleaching of kraft pulp. TAPPI J 80(10):263–268

Gleadow P, Hastings C, Warnqvist B, Barynin J, Schroderus S (1997a) Towards closed-cycle kraft – ECF vs TCF case studies. In: 1996 CPPA annual meeting, Montreal (winner of 1996 CPPA Douglas Jones Award for Best Environmental Paper)

Gleadow P, Hastings C, Richardsdon B, Towers M, Uloth V (1997b) Towards closed cycle kraft pulping: Canadian mill studies. PAPRICAN miscellaneous report 353. Pulp and Paper Research Institute of Canada

Glenn J (1997) Paper mill sludge: feedstock for tomorrow. BioCycle [magazine] 38(11). Available through: ABI/INFORM Global database. Accessed 20 October 2011

Greenpeace (1990) No time to waste, broadsheet produced by Greenpeace Canada, Vancouver

Hanninen E (1996) Minimum impact mill. Pap Asia 12(1):24–29

Higachi R, Cherr G, Shenker J, Macdonald J, Crosby D (1992) A polar high molecular mass constituent of bleached kraft mill effluent is toxic to marine organisms. Environ Sci Technol 26(12):2413–2420

IIED (1994) The sustainable paper cycle. IIED, London

International Labour Organisation (1992) Social and labour issues in the pulp and paper industry. ILO, Geneva

Johnston P, Stringer R, Santillo D, Stephenson A, Labounskia I, McCartney H (1996) Towards zero effluent pulp and paper production: the pivotal role of TCF bleaching. Technical Report 7/96 Greenpeace Research Laboratories, Earth Resources Centre, University of Exeter, Exeter, UK Greenpeace International, Amsterdam

Juuti S, Vartiainen T, Joutsenoja P, Ruuskanen J (1996) Volatile organochlorine compounds formed in the bleaching of pulp. Chemosphere 33(3):437–448

Kondo, Tadahiro (1993) Japan's pulp and paper industry faces dramatic changes. Paper & Packaging Analyst, No 15, November 1993, Pira International, UK

Kookana R, Rogers S (1995) Effects of pulp mill effluent disposal on soil. Rev Environ Contam Toxicol 142:13–64

Kopponen P, Välttilä O, Talka E, Törrönen R, Tarhanen J, Ruuskanen J, Kärenlampi S (1994) Chemical and biological 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin equivalents in fly ash from combustion of bleached kraft pulp mill sludge. Environ Toxicol Chem 13:143–148

Kovacs TG, Tana J, Lehtinen KJ, Sangfars O (1995) A comparison of the environmental quality of ECF and TCF bleached plant effluent. In: Proceedings of the annual international non-chlorine bleaching conference, Amelia Island, 5–9 March 1995, paper 5-3, 26pp

Kujala A (2012). Papermaking sludges and possibilities of utilization as material, Lappeenranta University of Technology, Bachelor seminar of environmental technology

Lapierre L, Paleologou M, Berry RM, Bouchard J (1997) The limits of metal removal from kraft pulp by acid treatment. J Pulp Pap Sci 23(11):J539–J542

Larisch B, Duff S (1997) Effect of H2O2 and DTPA on the characteristics and treatment of TCF (Totally Chlorine-Free) and ECF (Elementally Chlorine-Free) kraft pulping effluents. Water Sci Technol 35:2–3

Liebergott N, van Lierop B, Nolin A, Faubert M, Laflamme J (1989) Modifying the bleaching process to decrease AOX formation, report. Pulp and Paper Research Institute of Canada, Pointe-Claire

Liebergott N, van Lierop B, Kovacs T, Nolin A (1990) Comparison of the order of addition of chlorine and chlorine dioxide in the chlorination stage. Tappi J 73:207–213

Lockie M (1996) Pulp producers: losing metal or resolve? Pulp Pap Int 39(10):44–46

Luthe CE, Uloth V, Karidio I, Wearing J (1997) Are salt-laden recovery boilers a significant source of dioxins? TAPPI J 80(2):165–169

Martin VJJ, Burnison BK, Lee H, Hewitt LM (1995) Chlorophenolics from high molecular weight chlorinated organics isolated from bleach kraft mill effluents. Holzforschung 49(5):453–461

McCubbin N (1989) Dioxin'89: a bit like the adventures in Alice and wonderland. Pulp Pap Can 90(11):17–19

McCubbin N (1996) Numerous recovery options offer solutions for mill effluent closure. Pulp Pap 70(3):181–193

McCubbin N, Sprague JB, Bonsor N (1990) Kraft mill effluents in Ontario. Pulp Pap Can 91(3):T112–T114

McDonough TJ (1995) Recent advances in bleached chemical pulp manufacturing technology. Part 1: extended delignification, oxygen delignification, enzyme applications, and ECF and TCF bleaching. Tappi J 78(3):55–62

Mckague AB, Carlberg G (1996) Pulp bleaching and the environment. In: Dence CW, Reeve DW (eds) Pulp bleaching – principles and practice. Tappi Press, Atlanta, pp 746–820

Monte MC, Fuente E, Blanco A, Negro C (2009) Waste management from pulp and paper production in the European Union. Waste Manag, 29(1):293–308

Munkittrick, KR, van der Kraak GJ (1994) Receiving water environmental effects associated with discharges from Ontario pulp mills, Pulp Pap, 95(5), Canada

NCASI (National Council of the Pulp and Paper Industry on Air and Stream Improvement) (1994) Technical bulletin #684. NCASI, New York

O'Connor B (1995) Review of guidelines pertaining to the land application of municipal of industrial solid residues in Canada. Miscellaneous Report 314, PAPRICAN

O'Connor B, Voss R (1992) A new perspective (Sorption/Desorption) on the question of chlorolignin degradation to chlorinated phenolics. Environ Sci Tech 26:556–560

Paleologou M, Thibault A, Wong PY (1997) Enhancement of the current efficiency for sodium hydroxide production from sodium sulphate in a two-compartment bipolar membrane electrodialysis system. Sep Purif Technol 11:159–171

Papercutz: PlanetArk (2008) The environmental impact of paper production. http://papercutz.planetark.org/paper/impact.cfm

Priha M (1991) Toxic characteristics of effluents from bleached Kraft pulp mills. In: Crossland Chris (ed) International conference on bleached kraft pulp mills: Technical and environmental issues, 4–7 February 1991, World Congress Centre, Melbourne, National Pulp Mills Research Program, CSIRO, Dickson

Pryke D (2003) ECF is on a roll: it dominates world bleached pulp production. Pulp Pap Int 45(8):27–29

Rabert W, Zeeman M (1992) Dioxins/furans: U.S. EPA ecological risk assessment for land application and disposal methods for paper pulp sludge. Chemosphere 25:7–10

Rappe C, Wagman N (1995) Trace analysis of PCDDs and PCDFs in unbleached and bleached pulp samples. Organohalogen Compd 23:377–382

Ritchlin J, Johnston P (1998) Zero discharge: technological progress towards eliminating Kraft pulp mill liquid effluent, minimising remaining waste streams and advancing worker safety. Reach for Unbleached Foundation, Comox, 51 pp. ISBN 0-9680431-2-7

Rosenberg C, Kontsas H, Jäppinen P, Tornaeus J, Hesso A, Vainio H (1994) Airborne chlorinated dioxins and furans in a pulp and paper mill. Chemosphere 29:9–11

Rothwell A, Éclair-Heath G (2007) A new approach to paper mill sludge. Waste & Resources Action Programme, Oxon

Ryynänen H, Nelson P (1996) Environmental life cycle assessment of some new methods for producing bleached pulps from Australian eucalypt woods. Appita 49(3):167–172

Saunamaki R (1995) Treatability of wastewaters from totally chlorine-free bleaching. TAPPI J 78(8):185–192

Simons HA (1994) Technical background information document on pulp and paper mill air emissions. H.A. Simons Ltd., p 5517A

Södergren A (1989) Biological effects of bleached pulp mill effluents, National Swedish Environmental Protection Board Report 3558, Solna, Sweden

Södergren A (1993) Bleached pulp mill effluents: composition, fate and effects in the Baltic Sea, Swedish Environmental Protection Agency, Report 4047, Solna, Sweden

Sodergren A, Adolfsson-Erici M, Bengtsson BE, Jonsson P, Lagergren, S, Rahm R, Wulff F (1993) Environmental impact of bleached pulp mill effluent – bleached pulp mill effluent composition, fate and effects in baltic sea. Environmental Protection Agency Report 4047. Sodergren A (ed) Arlow, p 26–46

Södra Cell (1996) Annual environmental report, Södra Cell, Sweden

Stauber J Gunthorpe L Deavin J Munday B Krassoi R Simon J (1995) Comparative toxicity of effluents from ECF and TCF bleaching of eucalypt kraft pulps. In: 49th APPITA annual general conference, 3–7 April 1995, Hobart, pp 483–490

Sundelin B (1988) Effects of sulphate pulp mill effluents on soft bottom organisms – a microcosm study. Water Sci Technol 20(2):175–177

Suntio LR, Shiu WY, Mackay DA (1988) A review of the nature and properties of chemicals present in pulp mill effluents. Chemosphere 17(7):1249–1299

USEPA (1998) Maximum Achievable Control Technology (MACT) I & II. Title 40, Chapter 1, CFR, Part 63

United States Environmental Protection Agency (U.S. EPA) (2002) Chemical releases and transfers: pulp and paper industry. Sector notebook. http://www.epa.gov/compliance/resources/publications/assistance/sectors/notebooks/pulppasnp2.pdf

Verta M, Ahtiainen J, Nakari T, Langi A, Talka E, Servos MR, Munkittrick KR, Carey JH, van der Kraak GJ (1996) The effect of waste constituents on the toxicity of TCF and ECF pulp bleaching effluents. In: Servos M, Munkittrick K, Carey J, Van der Kraak G (eds) Environmental fate and effects of pulp and paper mill effluents. St. Lucie Press, Delray Beach

Vice K, Carrol R (1998) The cluster rule: a summary of phase I. Tappi J 81(2):91–98

Vidal J, Soto M, Field J, Mendez-Pampin R, Lema JM (1997) Anaerobic biodegradability and toxicity of wastewaters from chlorine and total chlorine-free bleaching of eucalyptus kraft pulps. Water Res 31(10):2487–2494

Women's Environmental Network (1989) The sanitary protection scandal, London; and National Swedish Environmental Protection Board (1989); Dioxins: A Programme for Research and Action, Stockholm, Sweden

WRAP (2010) Environmental benefits of recycling 2010 update – SAP097 http://www.wrap.org.uk/downloads/Environmental_benefits_of_recycling_2010_update53016551.8816.pdf

Chapter 4
Minimum Impact Mill Technologies

Abstract The Minimum Impact Mill Technologies which can meet the environmental challenges of the pulp and paper industry are discussed in this chapter. These include Optimised wood handling; Dry Debarking; High Yield Pulping Process; Extended Modified cooking; Efficient Brownstock Washing/Improved Pulp Washing; Oxygen Delignification; Ozone bleaching; ECF and TCF bleaching; Fortification of extraction stages with oxygen and hydrogen peroxide; HexA Removal; Condensate Stripping and Recovery; Minimum SO_2 and NOx Emissions; Electrostatic Precipitators; Increase in the dry solids content of black liquor; Installation of scrubbers on the recovery boiler; Incineration of odorous gases in the lime kiln; Installation of low NOx technology in auxiliary boilers and the lime kiln; SNCR on bark boilers; Over Fire Air Technique on recovery boilers; Installation of improved washing of lime mud in recausticizing; Efficient Primary, Secondary and Tertiary Waste Treatment (in some special cases); Partial system closure; Minimum Power Consumption; Waste water Recycling and reuse.

Keywords Pulp and paper industry • Minimum impact mill • Wood handling • Dry debarking • High yield pulping • Extended modified cooking • Oxygen delignification • Ozone • ECF • TCF • HexA • Emission • SO_2 • NOx electrostatic precipitator • Black liquor • Scrubber • Recovery boiler • Odorous gases • Lime Kiln • SNCR • Over fire air technique • Lime mud • Recausticizing • Partial system closure • Waste water treatment • Recycling

Paper mills vary widely in their environmental performance, depending on their age, efficiency and how they are run. Minimum-impact mills are those that minimize resource inputs and minimize the quantity and maximize the quality of releases to air, water and land. Pulp and Paper industry can optimize their environmental performance by implementing the most advanced manufacturing technologies, the most efficient mill operations, and the most effective environmental management systems.

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A number of research programs focusing on minimum impact, sustainable, energy-efficient pulp and paper manufacturing have been undertaken, some of which continue today. Many of these where funded at national levels, and typically involved national pulp and paper research institutes. With the use of clean technology, the manufacturing processes can minimize pulp and paper products' impacts on climate change and water (European Commission 2001; Nilsson et al. 2007; Vasara et al. 2001; Gavrilescu 2005; Hitchens et al. 2001; RPDC 2004; Suhr 2000; Woodman 1993; Beca AMC 2004, 2006). Carbon dioxide emissions from the manufacturing process can be reduced by investing in new plants, retrofitting existing plants, heat recovery and increased paper recycling.

The American Forest & Paper Association has announced an ambitious set of sustainability goals for its member organizations to aim for by 2020. The goals for the industry cover several areas listed below:

- Including improved recycling rates
- Reducing greenhouse gases
- Increasing the amount of fibre procured from certified forest lands
- Better use of energy
- Lowering the number of injuries in the industry

Among the goals, the industry hopes to improve the rate of paper recovery for recycling by pushing the rate to 70 % or more. According to the American Forest & Paper Association, 63.5 % of paper in the United States was recovered in 2010.

The Minimum Impact Mill Technologies which can meet the environmental challenges of the pulp and paper industry are presented below:

4.1 Emission Reduced Wood Handling

Wood is one of the nature's valuable raw materials and is an indispensable source of pulp, paper and panel board. Wood handling is the very start of the processing chain in the mills. Trains or trucks are used to transport the wood in the mills. Logs are usually cut in the forests to a free length of 2–6 m. The incoming raw material is weighed at the mill gate, and the volume is also measured in some cases. The logs are discharged to the mill yard for intermediate storage or directly into the process by truck loaders. Some process layouts contain slashing decks, which enable the logs to be cut to certain lengths. Logs then are lifted towards the drum by the infeed conveyor. During cold periods hot water or steam is used in the infeed conveyor to de-ice the logs. This results in weakening of the bond strength between the bark and the wood, making the logs easier to debark (Hatton 1987). Then the logs enter the debarking drum. The drum is usually from 5 to 6 m in diameter and from 25 to 35 m long in tumble debarking. The logs are debarked in a drum, where they hit against the drum and each other causing the separation of the bark from the logs (Scheriau 1972). The bark and some wood material exit usually through bark slots in the side of the drum. Finally, the logs leave the drum through the closing gate at the discharge end. The position of closing gate mostly affects the filling degree of the drum, which means the proportion of the drum volume which is occupied by the logs. After that the logs are typically sprayed with water at the washing station. This is done to remove the remaining loose bark and other impurities. Stones are removed from the main material flow at the stone trap and metal detector stops the conveyor if fragments of metal are found, which are removed manually. The logs are then cut into chips by either a gravity or horizontal feed chipper. In some plants the short logs are separated from the main stream and chipped with a short wood chipper. The chips are transported by a conveyor belt first to chip piles and then to a screening device. In some cases it is performed in the opposite order.

Some chemical pulp mills store wood chips in piles for 45 days or more. During this period the resinous compounds (extractives) within the wood degrade by oxidative and enzymatic mechanisms. The pile of wood chips can become quite warm during the storage period. Storage for longer periods may reduce the pulp yield and also the pulp strength.

Chip uniformity is very much important for proper circulation and penetration of the pulping chemicals. Therefore, significant attention is paid to operational control and maintenance of the chipper. Chips between 10 and 30 mm in length, and 2–5 mm in thickness, are generally considered acceptable for pulping. The chipped wood is passed over a vibrating screen that removes undersized particles (fines) and the oversized chips are routed for rechipping. Usually, the fines are burned with bark as hogged fuel. But they can also be pulped separately in specialized "sawdust" digesters. Most mills, segregate the chips according to the chip length. Chip thickness screening has become important as mills realize the need to extend delignification and reduce bleach plant chemical demands. Since the kraft cooking liquor can only penetrate the chip to a certain thickness, both absolute chip thickness and thickness uniformity have a significant effect on delignification (Tikka et al. 1992). Thin chips can be easily cooked to lower kappa numbers. Uncooked cores from over-thick chips will lower the average kappa reduction of a cook. This will contribute to higher bleaching chemical demands. Many mills are now using screening equipment that separates chips according to thickness in order to improve thickness uniformity (Strakes and Bielgus 1992). 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 can also be burned in a power boiler with heat recovery (USEPA 1992). Table 4.1 shows the measures to reduce environmental impacts from wood handling.

The effluents to water from wood handling originate from the debarking drum and from any spraying of wood piles with water. By the use of dry debarking, effluent from debarking can be minimised. In spraying piles the amount of water should be minimised by control versus ambient temperature and humidity to match the evaporation of water from the piles. Contamination of soil and groundwater should be avoided by paving the wood yard area particularly the surfaces used for storage of chips and by using water collection systems. Further treatment of polluted water might be required, whereas nonpolluted water may not require any treatment. Some

Table 4.1 Measures to reduce environmental impacts from wood handling

Effluents to water
Minimise the generation of effluents by using dry debarking; Recycle bark press filtrate to the kraft process; Organise separation of solids in wood yard effluent before bringing it to secondary treatment or flocculation
When sprinkling wood piles with water, the flow should be controlled to minimise run off; for sprinkled wood piles water collection systems in the wood yard avoid discharge of organic substances (COD, toxicity)
Air emissions
Prevention of dust formation and wind drift from the wood yard area and from the chip piles
Solid waste
Bark and wood residues are contaminated by sand and stones. Minimise their amount by clean handling. Recover bark and fines
Energy use
Use bark and wood fragments as fuel or prepare their use for energy recovery. Strive for high dry content by pressing and drying for increasing the calorific value
Noise
Suitable layout and location of wood yard. Locate debarking drums, chippers and chip screens indoors if possible. Use of low noise trucks and band conveyors

Based on European Commission (2013)

dusting of wood fragments from the chips and chip piles will occur and also from the wood yard area itself. This is normally a very local issue and seldom of any consequence outside the mill site. Wood and chip piles release volatile organic compounds (VOCs) originating from the extractives. No control measures for VOC reduction are applied in practice. Bark and any wood residues from the wood yard should be collected in a as dry and uncontaminated form as possible to use them as a fuel either in a bark or biofuel boiler at the mill or at a boiler with heat recovery outside the mill. In spite of the careful handling it is unavoidable that some of the material gets contaminated with sand and stones. Such material can often be used for soil improvement. The most important energy aspect in wood handling is to as efficiently as possible use the available residual biomass (bark, wood residue) to generate energy. Power use in the wood yard is commonly about 10 kWh per m^3 solid under bark of wood processed. This means about 25 kWh/tonne pulp for a mechanical pulp mill and below 60 kWh per tonne for a chemical pulp mill. Suitable dimensioning of the electric motors and motor controls should be used to keep power use low. Band conveyors provide a low power use alternative for chip transportation within the wood yard. There are many sources of quite high noise levels in the wood yard area such as from the debarking drum and the chippers. Ways to reduce the noise is primarily to locate this equipment in buildings or to construct noise protections. Trucks used in unloading and handling logs and chips are noisy in themselves. Noise in the form of impulse sounds is in addition created when logs are dropped onto piles or receiving tables. Purchase of low noise trucks and training in 'soft' driving are measures that should be applied. Noise protections may also be considered to shield receiving tables.

Since the wood raw material varies greatly depending on the location of the mill, the main challenge is how to handle these various species of wood in the right way. That means treating the raw material as gently as possible to make it perfect for further processing and to get the best possible yield. For this purpose, Metso Paper has developed a unique solution called ChipWay (www.ceeindustrial.com/public/data/companyCatalogue1224056297.pdf). This is their concept of wood handling, which incorporates all process stages and results in high quality chips in a way that saves wood. ChipWay features in-depth process know-how based on their wide experience, cutting-edge machine technology and embedded automation solutions. Besides being gentle to the raw material, ChipWay also pays special attention to the environment.

4.2 Dry Debarking

Debarking of the logs is usually the first process stage in pulp and paper mills. Debarking is required to separate the bark from wood, due to many adverse effects at the following process stages. The debarking drum does not operate in an ideal manner, and wood loss always occurs (Niiranen 1985). Wood loss depends mainly on the end product and the quality of the raw material which are mentioned below:

- Wood species
- Temperature (particularly below zero degrees)
- Cutting season
- Log freshness
- Dimensions of the logs

Koskinen (1999) has reported that normal wood loss may vary in the range 1–3 % whereas Agin and Svensson (1990) have reported that a wood loss of 5–6 % is normal. The end product mainly determines the requirements for the bark removal, which is usually measured by log cleanliness measurement system. Log cleanliness is defined as the percentage of the log surface that is bark-free after debarking. For groundwood pulp or thermo mechanical pulp (TMP) a log cleanliness of 98–99 % is usually required, but if the mill produces bleached softwood kraft pulp, then about 85–92 % log cleanliness is acceptable (Koskinen 1999). High bark removal requires a long residence time of logs in the drum and wood loss may become high. On the other hand, insufficient bark removal, saves raw material but it starts to increase the chemical consumption in chemical pulp making and detracts from the quality of the end product, particularly in the production of mechanical pulp. The debarking result is therefore a compromise between bark removal and wood loss. In the Finnish chemical pulp industry, the log cleanliness for softwood in particular is normally above 85–92 %, which is acceptable (Koskinen 1999). It is possible to reduce wood loss by aiming at a lower bark removal. This is emphasised when bark removal is already high and it is almost impossible to remove all the bark. However, if the processing is continued, wood loss will continue to increase. Moreover, a prolonged residence time of the logs in the drum increases the probability of their breaking.

The bark of the tree comprises about 10 % of the weight of the tree trunk. Bark is resistant to pulping, contains a high percentage of extractives, and retains dirt. Therefore it does not yield good papermaking material. In most pulping processes, bark is removed from the logs before they undergo chipping. Debarking drum is most commonly used, which removes bark by tumbling the logs together in a large cylinder. Slots in the outside of the drum allow the removed bark to fall through. The bark collected from these operations is usually fed to the hogged fuel boiler for generating 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 are discharged. Organic compounds like resin acids, fatty acids etc. and highly coloured materials leach out of the bark and go 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 using 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 debarking has gradually taken over wet debarking. In the dry debarking, the consumption of water, and hence the emissions of organic substances, are much lower. It is possible to eliminate emissions. In dry debarking, the bark that is used for energy production has a lower water content, enabling better energy balance (Nordic Council of Ministers 1993). Effluent from debarking is treated biologically. Use of biotechnically produced enzymes in debarking is under research (Bajpai 2012a).

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 (Jaakko Pöyry 1997; Finnish BAT Report 1997; SEPA-Report 4712-4 1997a). Although the process may increase the energy consumption, it results in better energy balance for the mill due to reduced water content of the barks, which are used for energy recovery. Effluent amounts and COD and BOD load is significantly reduced compared to wet barking – and this is often the main driver for installing dry debarking. Dry debarking can be applied in both new and existing mills and for most debarking purposes (softwoods, hardwoods) and for all pulping processes – mechanical pulping, chemical pulping etc. However, when producing high brightness TCF bleached sulphite pulps, wet debarking may be necessary because of quality reasons.

Raw effluents from a debarking plant are toxic to aquatic life. Biological treatment has proven 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 COD loading can be reduced up to 10 % (Salo 1999). The higher bark dryness in the boiler feed improves the energy efficiency. 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 solids removal systems for water has been applied with success. Dry debarking usually requires fresh wood in order 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 MEuros for a capacity of 1500 ADt/d pulp (European Commission 2001). Dry debarkers already dominate the industry, and wet systems have been in the process of being phased out since the 1970s (Smook 1992).

The conversion of an existing wet debarking system to a dry debarking system costs 4–6 MEuros. These costs include equipment and installation. Driving force for implementing this technique are that dry debarking decreases TSS, BOD and COD load as well as organic compounds like 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.

4.3 High Yield Pulping

For the production of various paper products, pulp fibres liberated from woody or non-woody biomass are used as raw materials. Two main concepts are adopted for fibre liberation. One is related to chemical action, which dissolves the native lignin that naturally binds fibres together. The dominant process of this type is known as the “kraft” process. The pulp yield for a typical kraft process is about 45 %. Another approach is mainly based on mechanical action to liberate the fibres; it is known as the high-yield pulping process, and its pulp yield typically is within the range 85–95 %. Bleached chemi-thermo-mechanical pulp (BCTMP), alkaline peroxide mechanical pulp (APMP), and preconditioning refiner chemical-treatment alkaline peroxide mechanical pulp (P-RC APMP) are referred to as high yield pulps (HYP) (Cannell and Cockram 2000; Zhou et al. 2005; Zhou 2004; Xu 2001; Reis 2001). The properties of HYP produced from the three different pulping processes are in general similar, depending on wood species, brightness levels and physical strength properties. Table 4.2 shows important feature of HYP.

HYP is in fact a cost-effective replacement for hardwood bleached kraft pulp in the manufacturing of printing and writing paper products. Hardwood HYP can impart fine papers higher bulk, stiffness, opacity, and better printability (Cannell and Cockram 2000; Zhou et al. 2005; Zhou 2004; Xu 2001; Reis 2001; Levlin 1990;

Table 4.2 Important feature of HYP

The production cost of high yield pulp is generally lower than that of chemical pulp
High-yield pulp is superior to chemical pulp in terms of light scattering, opacity, bending stiffness, and bulk. The presence of large amounts of fines also contributes to good sheet formation and surface smoothness, which can yield good printability
High-yield pulp has better recyclability than chemical pulp, due to less fiber hornification of the pulp
The fast-growing hardwood species such as popular are most suitable for the BCTMP and PRC-APMP processes
Due to wood shortage, a yield of about 90 % is indeed a considerable advantage

Ford and Sharman 1996; Johnson and Bird 1991). Use of high-bulk HYP allows papermakers to make paper with the same caliper and stiffness with less pulp. Presently, papermakers are using about 10 % HYP pulp in wood-free paper grades. Potentially, up to 50 % HYP pulp can be used in most printing and writing paper grades, for both coated and uncoated papers. In addition to having high pulping yield and low cost, HYP has clearly different characteristics in comparison with bleached kraft pulp (BKP). Most of the lignin from wood remains in HYP pulp fibres causing the fibres to be relatively stiff and resistant to lumen collapse. On the other hand kraft pulp, being essentially lignin-free, contains very flexible, collapsed fibres. The rigid tube-like structure of HYP pulp fibres results in a higher bulk and generally lower bonding characteristics than BKP fibres. The refining process in HYP pulping produces a broad distribution of fibre sizes due to peeling and delamination along the length of fibres and due to some fibre breakage. Fibre fragments, fibre fibrils and fibrillated fibres give HYP pulp significantly higher specific area than BKP, which may influence certain papermaking operations like, filler retention, internal sizing and polymer adsorption. Furthermore, the physical and chemical properties of fibres (increased bonding, decreased bulk and opacity) are significantly modified in the alkaline hydrogen peroxide bleaching process in HYP pulp production (Holmbom et al. 1991; Gullichsen et al. 2000; Pan 2001; He et al. 2004a, 2006a). HYP contains much more anionic groups such as sulfonic and carboxylic groups and thus has a higher fibre charge density than BKP (Thornton et al. 1993; He et al. 2004b, 2006b). Also, the anionic trash content of HYP is significantly higher than that of BKP. These unique physical and chemical properties of HYP may affect the wet-end chemistry of the papermaking process when HYP is substituted for BKP.

Today, kraft pulping is the dominant pulping process around the globe. However, in China, there has been a rapid increase in the production of high-yield pulp. For example, during the years 2000 to 2010, China's high-yield pulp production increased from about 500,000 to 4,500,000 t/a (Bräuer et al. 2012). This marked increase was caused by the huge domestic expansion in paper production/consumption and the enormous demand for pulp (Jerschefske 2012). In China, the hardwoods (poplar and eucalyptus), are the main raw materials for producing high-yield pulp. To date, China has become the largest producer of high-yield hardwood pulp, using both the BCTMP and the PRC-APMP processes, with the newly installed production lines being predominately based on the PRC-APMP process (Bräuer et al. 2012). The production of high-yield pulp in China has increased considerably in the recent years. The well-known advantages of this type of pulp include low production cost, high opacity, and good paper formation. In the context of state-of-the-art technologies, China's high-yield pulping, which is dominated by the PRC-APMP process, has a much higher energy input but a significantly lower wood consumption as compared to the kraft pulping process (Yanhong et al. 2015). If the saved wood in the forest or plantation is considered as an increment of carbon storage, then the carbon dioxide emission from the production of high-yield pulp can be regarded as much lower than that of kraft pulp. High-yield pulp can offer a significant environmental advantage of having a lower carbon footprint than kraft pulp, based on the assumption that wood saving from high-yield pulping (over kraft pulping) is considered as a repository of carbon storage.

A bilateral research team, bringing together scientists from FP Innovations with their industrial and academic partners from Canada and China, leveraged more than $1 million to develop a new HYP destined to meet this objective. The team's laboratory and mill trials have so far shown that current market high-yield pulp substitution levels can be increased up to 40 % in paper furnish without any significant negative effect on paper quality such as paper physical strength properties and printability.

Concerns over end product quality and paper machine operations have been limiting the use of HYP for the last three decades. HYP is gaining increasing interest for the production of high-quality wood-free paper grades as it is now known that HYP provides lower furnish cost, better printability and improved paper bulk and opacity. HYP is also environmental friendly due to its higher yield and lower carbon footprint in manufacturing process as compared to kraft pulp. This translates into less trees and chemicals per ton of paper, meaning a more cost competitive product and overall reduced environmental footprint. Researchers are now exploring to improve some of HYP properties, develop better paper coating and calendaring strategies, and reduce/eliminate the negative effect of HYP on wet-end chemistry.

4.4 Extended or Modified Cooking

Extended delignification addresses environmental issues and improve mill energy efficiency and has received wide use in the pulp and paper industry. Extended delignification is performed before the bleach plant to reduce the lignin content in the pulp entering the bleach plant in order to reduce the use of the bleaching chemicals. Reduction in the use of bleaching chemicals reduces the amount of pollutants discharged and increase the amount of organic substances going to the recovery boiler. New cooking methods have been developed which allow more selective delignification and provide mills with new pulping options. Mills are able to cook to lower kappa numbers, allowing less bleach chemical usage or permitting alternative bleaching methods. Mills can also maintain kappa numbers while improving yield and physical strength properties.

Table 4.3 Modified cooking principles

High initial hydrosulfide ion (HS-) concentration
Even alkali (OH-) profile
Low concentration of dissolved solids in the liquor
Low initial and final temperature
High initial ratio of HS- to OH

In the late 1980s modified cooking was introduced and all new fibreline mill projects applied it. Modified cooking refers to a variety of techniques that have been developed in the last two decades to modify the conditions in kraft digesters so that the kappa number can be reduced while minimising loss of strength properties and yield. The extended delignification through modified cooking uses the principle of alkali concentration profiling. The alkali concentration is kept lower at the beginning of the cooking (in impregnation) and is increased towards the end of the cook. This allows cooking to reduce the residual lignin contents without undue degradation of carbohydrates or excessive loss of pulp strength thus reducing the delignification demand in the bleaching plant and its environmental load. Table 4.3 shows modified cooking principles. These principles are applied in different ways and to various degrees in case of both modified continuous cooking (MCC) and modified batch cooking (MBC).

4.4.1 Batch Cooking

There are different types of batch extended delignification systems available:

- Rapid Displacement Heating (RDH)
- SuperBatch
- Enerbatch.

In the RDH and Superbatch processes, impregnation with black liquor is performed to decrease the heat consumption and at the same time to increase the initial sulphide concentration and decrease the effective alkali charge (Bowen 1990; Barratt 1990). Developments in SuperBatch® cooking have focused on the cooking technology and chemistry that yield the highest possible strength. The SuperBatch system allows the extension of cooking to very low lignin contents without any process modifications and without losing pulp strength. Today, we are able to produce pulps that not only meet stringent pulp requirements, but also due to effective impregnation stages and high chip quality improve the operation of the following stage, i.e. the knotting and screening process. SuperBatch cooked pulps can also improve profitability in papermaking process by enabling higher machine speeds. There are several installations of SuperBatch cooking plant world wide.

In the Enerbatch process, a pretreatment with white liquor followed by a pretreatment with black liquor is performed. All these displacement cooking processes show significant energy saving and an improved pulp quality. The lignin content is usually measured as the kappa number with a standardised method. In all these modified batch cooking methods, chips are impregnated in the digester before the bulk delignification that is proceeded by an alkali concentration profile. In displacement batch cooking the heat in the spent cooking liquor is recovered by displacing it from the digester with a washing liquid and using it to preheat chips in the next cooking batch (impregnation).

There are limitations in case of conventional cooking regarding how low the kappa number can be brought without affecting the pulp quality. This kappa number is around 30–32 for softwood and 18–20 for hardwood. By 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 maintaining the yield and strength properties. The kappa reduction depends beside others on the modified cooking technology applied and whether a retrofitted or new installation is used.

Several mills in the world with conventional batch cooking installations have rebuilt their conventional batch cooking plants to modified batch cooking systems. Modified batch cooking includes liquor displacement stages in the cooking cycle. Most new batch cooking installations are modified batch cooking installations. The advantages of the modified systems are better heat economy, improved pulp quality and less rejects. The modified batch cooking system consists of several batch digesters and a tank farm. The production rate determines the number and size of digesters. The tank farm consists of hot liquor (black and white) accumulators, tanks for impregnation and displacement liquors and soap separation, and a pulp discharge tank. Intermediate black and white liquor accumulators are essential for balancing the flows between different cooking stages. Several heat exchangers recover heat from the hot liquors.

In the modified system, after cooking, the digester is cooled by displacement with cold wash liquor. The hot displaced liquor is taken to a pressurized tank. After cooling, the pulp suspension is pumped, out of the digester at a low consistency. The hot liquor is reused in the cooking cycle to heat up the digester after impregnation liquor fill. White liquor can be added both to the impregnation fill and the hot liquor fill. Compared to conventional batch cooking, a tank farm is needed in the modified system to store the different liquors between the digesters. Depending on the displacement batch process (RDH, SuperBatch, Cold Blow or Enerbatch), there are some differences in the cooking cycles, displacement liquors and tank farm configurations, but the principles are similar. The digesters are heated at the beginning after filling by using hot displacement liquors, and the cook is ended with a cold displacement before discharging by pumping. In a conventional cooking system, more time is needed to heat the digester than in modified cooking. In displacement cooking, the cook is brought to a high temperature in the relatively short hot liquor fill or displacement stage. The digester is at a high temperature for a longer period and a lower cooking temperature can be used. Furthermore, the alkali profile can be adjusted and controlled in the different stages of cooking in the modified system. A higher residual alkali can be used at the end of the cook as the displaced cooking liquor containing considerable amounts of alkali is reused in the next cook as hot liquor fill. The longer cooking time at a lower temperature and the higher residual alkali level at the end of the cook give several advantages with respect to pulp quality. The chips are cooked more homogenously, the kappa number deviations inside the digester are reduced and less reject is produced. The strength properties of pulp produced by displacement batch cooking as compared to conventional batch cooking is improved. There are several reasons for this improvement in pulp quality, the main reasons being gentler blowing after cooking, more uniform cooking, high residual alkali at the end of cook and lower cooking temperature. There is sufficient automation in the modern displacement cooking plants and a computer system controls the entire operation. The control system includes controls at basic (distributed control system) and supervisory levels.

4.4.2 Continuous Cooking

Continuous digesters are being used in modern kraft pulping. Continuous kraft cooking was the standard until the 1980s, but in the middle of the 1980s, the breakthrough of modified continuous kraft cooking occurred and the technology has since been developed further. The major principles of modified kraft cooking that distinguish it from conventional kraft cooking are: the split white liquor charge, prolonged delignification by using the washing zone for delignification and the use of counter-current cooking at the later part of the cook because it was thought at that time that the concentration of dissolved lignin and sodium ions in the liquor should be as low as possible, particularly in the final phase of the kraft cook (Axegård et al. 1978; Nordén and Teder 1979; Teder and Olm 1981; Kubes et al. 1983; Sjöblom et al. 1983; Johansson et al. 1984). The introduction of split alkali charge actually reduces the hydroxide ion concentration at the beginning of the cooking process, which reduces the carbohydrate loss and increases the hydroxide ion concentration at the end of the kraft cooking process. This in turn enables the transformation of the slowly reacting residual-phase lignin to react like the faster bulk-phase lignin (Lindgren and Lindström 1996). The use of the modified kraft cooking principles made it possible to reduce the temperature of both continuous kraft cooking and batch cooking systems. The major benefits of modified kraft cooking are improved yield and selectivity (drop in limiting viscosity number versus reduction in kappa number) (Andbacka and Svanberg 1997). The first continuous cooking application on the market that adapted split white liquor charge and counter-current cooking was named Modified Continuous Cooking (MCC) and developed by Kamyr. Later, similar industrial continuous cooking concepts were established, such as Extended Modified Continuous Cooking (EMCC) by Alström, Iso Thermal Cooking (ITC) by Kvaerner Pulping and Lo-Solids by (Alström/Andritz) (Kubes et al. 1983; Sjöblom et al. 1983; Johansson et al. 1984; Andbacka 1991). Modified continuous kraft cooking was later improved by black liquor impregnation, where black liquor was withdrawn from a later part of the digester and charged into the impregnation phase at the start of the cooking process. The idea of using black liquor recirculation during continuous cooking was adapted from the batch cooking systems. The initial sulfide ion concentration thus increased significantly, which led to faster degradation of the initial-, bulk- and residual-phase lignin. Although high sulfidity is advantageous from a chemical delignification point of view, the sulfidity charge is also regulated in practice by discharge limits. Black liquor contains organic matter which when present during the impregnation phase have been shown to have a rate-increasing effect on bulk-phase delignification but a rate-decreasing effect when the final residual delignification phase dominates (Wedin 2012). To avoid severe carbohydrate loss, the kraft cook should thus be terminated before the even slower residual phase begins to dominate, example by terminating the cook at a higher kappa number. The positive effect on the bulk phase has been related to lignin structures having free phenolic groups (Sjödahl et al. 2006).

At the end of the 1990s, a new application called Compact Cooking, was marketed and supplied by Kvaerner. Compact Cooking used black liquor recirculation in a continuous cooking system, It was carried out using a significantly simplified digester compared to that used in ITC consisting of two cooking zones used concurrently and two sieves for black liquor extraction. A separate impregnation vessel also became a standard in the Compact Cooking concept. This made it easier to decrease the temperature during impregnation. The alkali charge was split between two positions, as black liquor (adjusted with white liquor to the right concentration) to the impregnation vessel and as white liquor to the first cooking zone of the digester. After the first cooking zone, the black liquor was extracted and transferred to the impregnation. The recirculation of the black liquor made it possible to reduce the cooking temperature (without increasing the size of the digester) because it allowed for a higher hydroxide ion concentration through the entire cooking process. This resulted in an increased delignification rate and reduced amount of residual phase lignin (Lindgren and Lindström 1996). The implementation of black-liquor recirculation allowed for a decrease in temperature of approximately 10 °C for softwood and 5 °C for hardwood, which improved the yield and selectivity in comparison to ITC cooking. Another improvement in the Compact Cooking was the use of a higher liquor-to-wood ratio during impregnation. This was able to remove one of the most harmful alkali peaks for hemicellulose dissolution and degradation during kraft cooking. Table 4.4 shows modified continuous cooking systems.

The MCC process is based on two main principles. As compared with conventional cooking, the cook 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 cook. This is performed by splitting the alkali charge into different insertion points and by ending the cook in the counter-current 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 min retention. The con-current zone has a 60 min, and the counter-current zone has a 60 min. 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 counter-current zone. Two benefits are achieved by adding white liquor to the counter-current zone.

Table 4.4 Modified continuous cooking systems

MCC – Modified continuous Cooking (Kamyr)
EMCC – Extended modified continuous cooking (Kamyr Inc/ Ahlstrom)
ITC – Iso thermal cooking (Kværner Pulping)
BLI – Black liquor impregnation (Kværner Pulping)
Lo Solids – Lo solids cooking Ahlstrom/Andritz
CC – Compact cooking

Based on Headley (1996), Bowen (1990), and Andbacka (1991)

The initial hydroxide concentration is lowered. Some cooking is performed in the counter-current zone, where the dissolved solids are lower.

EMCC was a further development in extended cooking. The EMCC process further decreases the initial hydroxide concentration and increases the amount of cooking in the counter-current zone. 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 290–300 degF. Iso-Thermal Cooking (ITC) (developed by Kvaerner) expands on EMCC with an additional circulation loop and fifth white liquor addition point (Engstrom 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 back flushing valves which reduce blinding. The high circulation rates result in even more cooking in the counter-current zone. As compared with EMCC, the initial hydroxide concentration is reduced. The temperature in the digester is lower and nearly uniform throughout the digester. The amount of cooking in the counter-current 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 $3 million. To date, several digesters in Europe and Japan have been converted to ITC. One retrofit has been installed in North America in 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 min compared with 30 min for a conventional impregnation vessel. The major benefit observed with black liquor impregnation is a 10 % increase in tear.

Table 4.5 World market share of modified cooking processes

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

Based on data from Beca AMEC (2004)

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 cook 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.

The most recent cooking development concerns the extension of the impregnation process. A longer impregnation process at lower temperature improves the uniformity of the pulp and reduces the reject content of softwood (Karlström 2009). The Compact Cooking concept has adapted prolonged impregnation; it is marketed as Compact Cooking Generation 2 and supplied by Metso (CoC-G2).

Currently there are several continuous and batch digester systems with modified cooking worldwide, capable of producing about several thousand ADt/d of pulp. Modified cooking capacity increased more than fivefold during the 1990s, but has tapered off in recent years. Table 4.5 shows the market share of the various systems offered, based on system capacity.

4.4.3 Modifying Kraft Pulping with Additives

The era of modified kraft pulping originally called extended delignification which began in the 1980s was founded on chemical principles intended to make kraft pulping more selective for delignification over polysaccharide degradation. At present, available pulping technologies like MCC, EMCC, RDH, Superbatch require extensive retrofitting or digester replacements. So, their usefulness is limited if capital investment 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 as a pulping additive has become a simple and practical approach to overcome the above concerns. Other chemicals like polysulfides and surfactants are also becoming strong candidates to be considered as pulping additives during kraft pulping (Borchardt et al. 1997; Bajpai et al. 2005). Digester modifications and pulping additives do not work antagonistically but are complementary.

4.4.3.1 Anthraquinone

Anthraquinone (AQ) and a few closely related compounds can act as redox (reduction-oxidation) catalysts for alkaline pulping (Fig. 4.1). Very small amounts of AQ are enough. AQ, increases the delignification rate in a soda cook and also to a smaller extent in a kraft cook (Holton 1977; Fleming et al. 1978; Löwendahl and Samuelsson 1978; Fullerton and Wright 1984; Dimmel 1995; Quinde et al. 2004). AQ stabilises the carbohydrates by oxidising their reducing end groups (Obst et al. 1979) and thereby protecting them against the peeling reactions which lead to a decrease in pulp yield. In this reaction, AQ is itself reduced to anthrahydroquinone (AHQ), which can cleave β-O-4 linkages in the lignin. Different reaction mechanisms have been suggested for the lignin degradation caused by AHQ. Both an ionic mechanism (Aminoff 1979; Obst et al. 1979; Gratzl 1980) and a radical mechanism

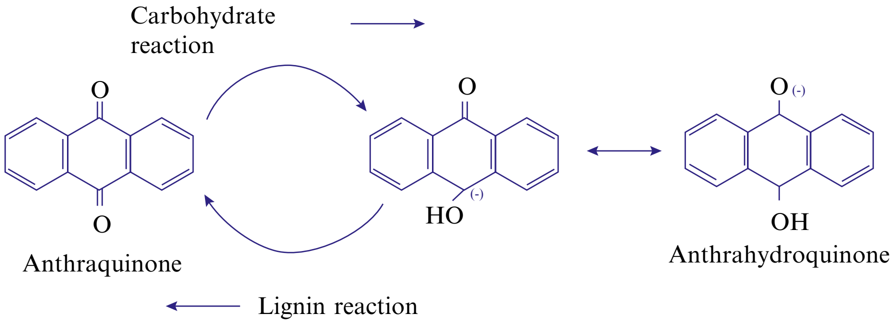


Fig. 4.1 AQ catalytic cycle

(Dimmel and Schuller 1986) for the β-arylether cleavage have been reported. The AQ acts almost like a catalyst during the kraft cook, as about 20 % of the AQ can be found in the black liquor after the kraft cook (Laubach 1998; Goyal 1997; Ahluwalia et al. 1992). AQ can be used in the soda-AQ process, but its main use today is as an additive in the kraft process, mainly in countries with high raw material costs such as Japan. A major disadvantage of the addition of AQ, apart from the price, is that the bleachability i.e. the amount of bleaching chemicals required to reach a given brightness for a given lignin content of the unbleached pulp, decreases when AQ is added to kraft or soda cooks (Håkansdotter and Olm 2002).

The addition of 0.5–1 kg AQ/t wood to a standard kraft cook results in a 4–6 kappa number reduction 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 required since AQ and sodium sulfide 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.

4.4.3.2 Polysulfide

Polysulphide is another additive that has been examined by several researchers (Kleppe, and Kringstad 1963; Teder 1968). The polysulphide has a positive effect both on the delignification rate (Lindström and Teder 1995) and on the carbohydrate stability, as it oxidises the carbohydrates, reducing the end groups to alkali-stable aldonic acid end groups (Teder 1968; Pekkala 1982, 1986; Jiang 1993, 1995; Katz 1993). The positive effect of polysulphide on the delignification rate is evident at concentrations of 0.02 mol/dm^3 and higher (Berthold and Lindström 1997). Even though polysulphide is formed during the kraft cook, most of it rapidly decomposes at temperatures higher than 110 °C. Without polysulphide addition, the concentration of polysulphide is lower than required to achieve the positive effect on the delignification rate (Gellerstedt 2003). Because of this, polysulphide has to be added to the cooking liquor. The drawback of polysulphide addition is that the amount of sulphur in the system is increased, and this disturbs the sodium-sulphur balance in the mill, thereby generating higher emissions to the atmosphere.

Polysulfide pulping is a variant of kraft pulping in which half or more of the sodium sulfide of kraft white liquor is first oxidised. 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 15–18 kappa range with final yield and strength properties comparable to those from conventional kraft brown stock at about 30 kappa number (Jiang 1995). Kraft polysulfide pulps have different papermaking characteristics due to the retention of hemicelluloses, and may be undesirable in some paper grades. 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.

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.

4.4.3.3 Sodium Borohydride

A preliminary report on the use of sodium borohydride in kraft pulping was published by Hartler in 1959. The results of this study revealed that sodium borohydride increases the pulp yield. Subsequently, investigations in the 1960s and 1970s showed similarity with the results of Hartler (Pettersson and Rydholm 1961; Meller 1963; Aurell and Hartler 1963; Annergren et al. 1963; Meller and Ritman 1964; Gabir and Khristov 1973; Diaconescu and Petrovan 1976). In the last decades, some investigations focused on feasibility of using boron compounds with different species and additive ratios in pulp and paper industry (Istek and Gonteki 2009; Tutus 2005). Sodium borohydride, has a reducing effect on the carbohydrate end groups and makes them alkali-resistant (Hartler 1959). This gives an increase of 3 percentage points in the softwood pulp yield. It is mainly glucomannan that accounts for this yield increase. At the same time, the amount of xylan in the pulp decreases. This is probably due to a decrease in the xylan adsorption onto the fibres as a result of the higher amount of glucomannan. Sodium borohydride is today not used commercially, as it is too expensive. Adding of sodium borohydride to cooking liquor increases pulp yield through greater retention of hemicelluloses. Sodium borohydride causes reduction of the carbonyl group located on the end group of cellulose to a hydroxyl group during the cooking and stops the probable peeling reaction because it is a powerful reducing agent. Thus, a decrease in yield during cooking can be prevented. This reaction can occur in both cellulose and hemicellulose (Courchene 1998). The peeling reaction initiated in carbonyl groups in the end units is prevented by the conversion of carbonyls to hydroxyls by borohydride. The major effect of borohydride is to prevent the acceleration of glucomannan removal that otherwise occurs at 100 °C (Tutus and Usta 2004).

4.4.3.4 Surfactants

The first patent on the use of non-ionic surfactants as additives on pulping dates from 1975 (Parker and Lundsted 1975). Surfactants help the penetration of the cooking liquor by wetting and emulsifying the wood extractives. However, it should also be considered the wetting effect on the chip surface and improved penetration of the liquor into the interstices of the chip. 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) (Chen 1990, 1994). 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.

Surfactants as surface active chemicals are very effective at very low concentrations. Usually they are applied at 0.025–0.06 % based on o.d. wood. The dosage will depend on the degree of delignification and the target kappa number must be based on the capacity of rejects 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 extractives composition, attempts have been made to favorably alter this ratio during pulping. A common operation when pulping hardwoods (they lack of 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 upon 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 less problems related to pitch than hardwoods. This phenomenon can be explained because of the emulsifying action of the resin acids (Quinde 1994).

4.4.3.5 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. 4.2.

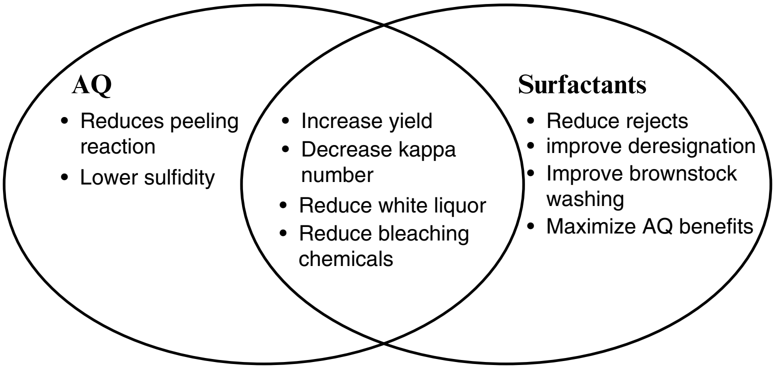


Fig. 4.2 Benefits of using anthraquinone and surfactants

4.4.3.6 Combination of AQ-Polysulfide

It has been proved that the combination of anthraquinone and polysulfide give more yield gains than the sum of respective yield increase. This augmentation is called the synergistic yield increasing effect of polysulfide and anthraquinone (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.

4.5 Efficient Brownstock Washing/Improved Pulp Washing

About half of the wood is dissolved in the digester. The pulp coming from the digester contains both fibres and spent cooking liquor (black liquor). The black liquor contains inorganic chemicals and a large amount of organic compounds contributing to BOD, COD, colour and conductivity in the effluent. The black liquor from the pulp is removed in the subsequent washing stages and fed to the chemical recovery system, where cooking chemicals and energy are recovered (Bajpai 2008a). The dissolved organic compounds together with the spent cooking chemicals are separated from the cellulose fibres in the brown stock washing stages. The main objectives in brown stock washing are to achieve:

- The cleanest pulp while using the minimum amount of water.
- A high solids concentration in the weak black liquor fed to the evaporators.

In chemical pulping, the main reason for brown stock washing is to remove soluble impurities using a minimal amount of water (as this water must be evaporated later on). Pulp is also washed to recover valuable cooking chemicals and organic chemicals, which are recovered for their heating value (Crotogino et al. 1987). Efficient washing improves the recovery of spent chemicals, reduces the consumption of reagents in the subsequent bleaching and limits effluent load from the plant (Tervola and Gullichsen 2007). It also has a positive effect on pulp quality and prevents deposition problems (Wilson 1993). The brown stock washing system is always mill dependent. It starts with cooking (Hi-Heat) and is followed, mainly in series, by various equipments such as a Drum Displacer (DD), a vacuum filter, a diffuser, a press filter, which use either dilution/thickening or displacement washing principles or their combination. The target is to connect these different washing equipments in a series and obtain as good a washing result as possible with a minimum amount of used wash water (Crotogino et al. 1987). Brown stock washing also plays a key role in oxygen delignification performance. Washing before oxygen delignification is important, because a high incoming wash loss into the oxygen delignification reduces pulp strength and consumes oxygen and alkali. Washing after oxygen delignification is also very important, as it reduces the amount of detrimental organic wash loss and cooking chemicals entering bleaching. When the amount of washing loss is high in the bleaching feed, more bleaching chemicals are consumed. With washing after oxygen delignification the economy and the environmental friendliness of the whole fibreline is improved (Andbacka 1998).

Examples of washers with excellent washing efficiency at low dilution factor (ratio of wash water used to pulp washed) are:

- Compaction baffle filter
- Atmospheric diffusion washers
- Pressure diffusion washers
- Pressure drum washers
- Displacement (twin roll) wash presses
- Drum displacement (DD) washer (multi-stage)

The discharge consistency is highest for wash presses. Wash presses and diffusion washers are especially effective in the removal of dissolved organic compounds. Wash presses have become more common, especially as the last washing stage before bleaching.

The pulp is then screened with pressure screens. The screen room may be located before or after the oxygen delignification stage. Most mills screen the pulp before oxygen delignification, but there are many mills where the screen room being located after the oxygen delignification stage. Modern screen rooms are closed operations, i.e. without a continuous process effluent discharge during normal operating conditions. In practice there typically is a small discharge due to, for example, pump seal water, drainage from screening rejects, and minor leakage from piping and equipment. A key principle in such an operation is that any water entering the process must leave either with the unbleached pulp or with the weak black liquor fed to the chemical recovery system. Closed fibreline operation requires that the volume of water entering the system be as small as possible to reduce both capital cost and operating cost (as steam) for evaporation. Key components of the closed fibreline include adequate brown stock washing capacity, closed screening, control of water inputs and effective process controls (Stratton and Gleadow 2003).

Most of the 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 fibrelines, 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 mentioned above. Efficient washing reduces the carry-over 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 idea is to bring the clean counter-currently through the fibreline, which gradually increases the dry solid content of the liquor.

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 in order 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 Europe and North America, closed screening and brown stock washing is reality in almost all mills.

In many pulp mills the washers are equipped with basic instrumentation and the individual control loops are supervised by a DCS system. In most cases, the coordination of these individual control loops is done manually by the operators. In any manual operation the results vary with the individual, so the stability of the whole operation suffers. The transition periods during fibre species and production rate changes can be particularly troublesome. Many mills are now realizing that poor performance in the washing line can have a significant effect on the stability of operation and the production costs in other related processes pulping or recovery process. For example, poor washing of the pulp can result in higher bleaching chemical consumption. Organic materials that are not washed out of the pulp are a lost source of energy for the recovery boiler. On the other hand, if the filtrate liquor is too dilute, evaporation costs will be higher. In some cases this may result in a production bottleneck for the whole pulp mill. Also, if outlet consistency is not regulated and becomes too high the washer operation may be halted. The operation of the brown stock washing operation is therefore a delicate balancing act, with the operators trying to achieve the best removal of soluble impurities, the highest possible outlet consistency and the highest solids content in the dilute liquor sent to the evaporation plant. But operating practices vary from operator to operator and, in some mills, the wood species and production rates change on a regular basis, thereby destabilizing the washing process. Because the washing line is a sequential, countercurrent operation, the stability of the whole line can be upset. It may take only a few minutes to destabilize, but the recovery may take several hours. To address these issues Metso Automation has introduced a whole-line optimization control called DNAwash, which controls first the individual washing units and then balances the distribution of washing liquors and manages filtrate tank levels throughout the entire line (Kapanen and Kuusisto 2002). Most importantly, this control manages the washing operation through transitions between fibre species and during the usual production rate changes. The benefits of improved washing line control and optimization include: optimized washer load distribution; consistent operation; no human errors; lower more stable washing losses; steam savings in evaporation plant; more even pulp quality and reduced bleaching chemical use; alleviation of bottlenecks and higher production rates; more pulp with the same equipment. Stora Enso Fine Paper's Veitsiluoto mill, in Kemi, Finland invested in Metso Automation's DNAwash, implemented in their metso DNA control system to realize many of these goals (Williamsson and Kapanen, 2005).

4.6 Oxygen Delignification

Oxygen delignification of pulp is a proven technology which has been in use for more than four decades. In most cases, the term is used synonymously with oxygen bleaching. The use of oxygen delignification systems is increasing throughout the world (Genco et al. 2012). Oxygen was recognized as a potential bleaching agent as early as 1867, at which time a process was patented to improve pulp bleaching by running "heated air through an agitated pulp suspension". Because of the trend in the industry towards ECF bleaching combined with minimal emission of chlorinated organic compounds, oxygen delignification has emerged as a very important process. Oxygen delignification can be used successfully to delignify kraft softwood and hardwood pulps, sulphite softwood and hardwood pulps, and nonwood pulps. These pulps are used in a wide variety of products, including printing and writing papers, copy paper, newsprint, grease proof paper, paper board, tissue, and diapers.

The 'oxygen stage' was developed in the late 1960s when serious concerns about bleach plant effluent discharges, pollution control and energy consumption began to surface. These concerns were originally directed at reductions in BOD, COD and colour. The major areas of growth for oxygen delignification initially were Sweden in the 1970s and Japan in the 1980s, in order to save bleaching chemical costs. The late 1980s saw a widespread growth due to the chlorinated organics issue. For TCF production, oxygen is essential to obtain a major decrease in lignin prior to the bleach plant. The choice of oxygen delignification is based on economical, technical and environmental needs at a particular mill. The worldwide installed capacity of oxygen delignified kraft pulp in 2010 was estimated (Genco et al. 2012) at about 300,000 metric tons/day, representing most of the world's bleachable grade pulp.

Oxygen delignification involves an extension of the delignification started in the cooking process and provides the bleaching plant with a pulp that has a significantly reduced kappa number. The primary advantages of oxygen delignification coupled with modified bleaching over conventional bleaching include:

- Partial replacement of chlorine based chemicals (especially chlorine gas) for ECF pulp production
- Elimination of all chlorine based chemicals in TCF sequences
- Retainment and the recycling of the extracted organics and chemicals applied in the oxygen stage
- Incineration of the recycled organics to generate energy;
- Energy savings

Oxygen production requires only 12.5 % the energy of chlorine dioxide expressed as equivalent chlorine (McDonough 1990, 1995; McDonough and Herro 1997; Simons and AF-IPK 1992; Nelson 1998; Jones 1983; Gullichsen 2000; Pikka et al. 2000; Tench and Harper 1987). Most American and Canadian mills apply oxygen delignification to assist in the economics of bleach plant modernization or expansion, although more and more interest is being placed on the reduction of environmental pollutants (Tatsuishi et al. 1987; Enz and Emmerling 1987). In 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. Oxygen delignification significantly improves bleach process efficiency and can shorten a bleaching sequence provided that effective washing is used after the oxygen stage. Because less lignin enters the bleach plant, there is a significant decrease in consumption of bleaching chemicals and a reduction in cost because oxygen is less expensive than chlorine dioxide and hydrogen peroxide.

Oxygen delignification, is done as the first bleaching stage after kraft cooking to reduce the kappa number by 45–65 %. The effluent from the oxygen stage can be recovered and taken to the recovery boiler by integrating the oxygen stage into the brown stock washing system. The oxygen delignification stage is a more selective way to delignify the pulp than to extend the cooking to low kappa numbers. There are, however, viscosity and pulp strength losses also related to oxygen delignification, which is why the oxygen stage cannot be extended to too low kappa numbers. Figure 4.3 shows how the oxygen stage is integrated into the brown stock countercurrent washing system. The pulp is washed after cooking to reduce the amount of dissolved material from cooking entering the oxygen stage. The pulp is mixed with alkali and oxygen. Steam is added to increase the temperature to 90–110 °C. After delignification and bleaching in the pressurized reactor, the pulp is discharged to a blow tank where gases are separated out. After oxygen delignification and gas separation, the pulp is washed to recover the used chemicals and the dissolved organic material, corresponding to a yield loss of 2–4 % of the pulp flow.

Oxygen may be classified as an oxidizing agent with low reactivity, moderate selectivity, and low efficiency. It has moderate ability to bleach shives and other particulate matter and most significantly has low impact on the environment. The

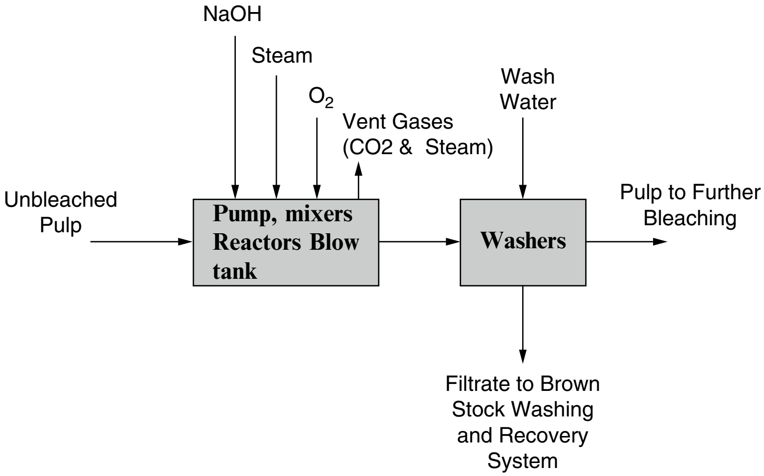


Fig. 4.3 Incorporation of the oxygen delignification stage in brownstock washing and cooking liquor recovery cycle (Based on McDonough 1996; Gullichsen 2000)

low reactivity necessitates elevated temperatures (85–115 °C) and pressures (4–8 bars) for oxygen delignification reactions to proceed. Oxygen's moderate selectivity can sometimes lead to appreciable loss in pulp viscosity and may necessitate adding a viscosity protector such as magnesium sulphate to the pulp in the case of softwood. Low efficiency means that appreciable quantities of the reagent must be added to the oxygen delignification system (15–25 kg O_2 per tonne of pulp).

Two types of systems are used commercially for oxygen delignification; these are generally characterized as high- and medium-consistency systems. Figures 4.4 and 4.5 show flowsheet and equipment of typical medium consistency oxygen delignification; Fig. 4.6 shows flowsheet of typical high consistency oxygen delignification and Fig. 4.7 shows the reactor for high consistency oxygen delignification.

Because of better selectivity and lower investment costs, the medium consistency (MC, 10–15 % consistency) system has dominated mill installations since the early 1990s (European Commission 2001) but high consistency installations (HC, 25–30 % consistency) are in use as well. Table 4.6 shows typical operating data ranges for Oxygen Delignification Process. Figure 4.8 shows the flow sheet of a typical two-stage oxygen-delignification installation.

The OXYTRAC system (Bokström and Nordén 1998) is an example of a modern two-stage oxygen delignification process system. The first installation of this design was at SCA's Östrand mill in Sweden. Very high delignification degrees, approximately 70 %, have been achieved through optimization of the system. It is claimed that chemical consumption has been reduced and pulp quality improved with better selectivity than with the single-stage oxygen delignification this system replaced. The OXYTRAC design utilizes two reactor stages (Fig. 4.9) (Alejandro and Saldivia 2003). The first operates at high chemical charge and pressure (8–10 Bar) but at relatively low temperature (85 °C) and with a short retention (20–30 min). The high

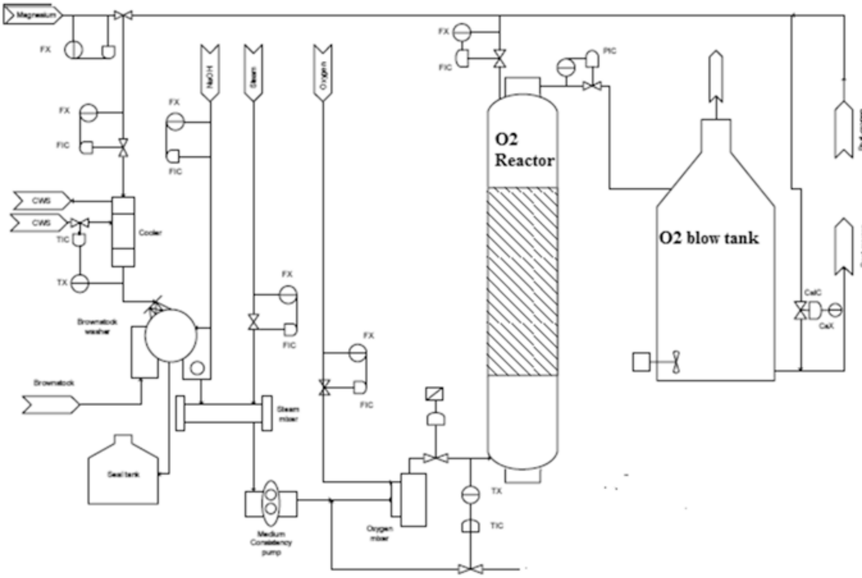


Fig. 4.4 Flowsheet of typical medium-consistency oxygen delignification

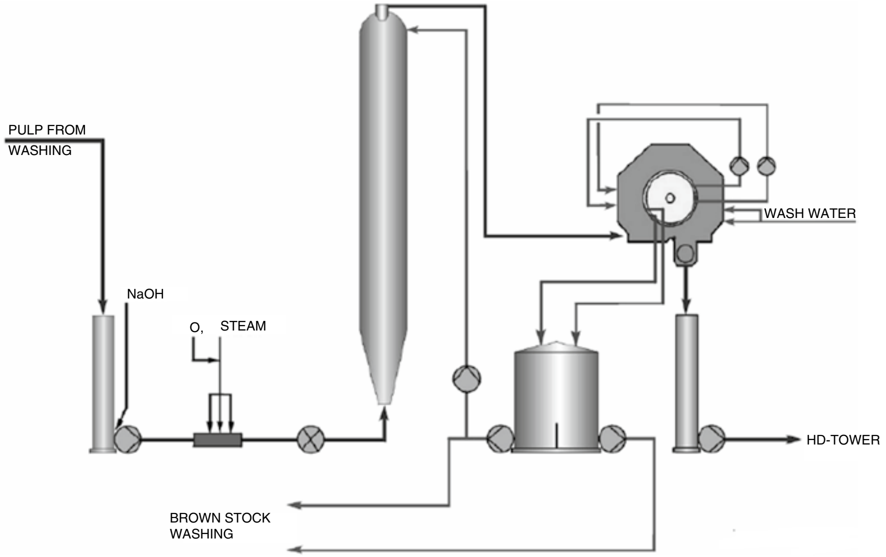


Fig. 4.5 Equipment of medium consistency oxygen delignification

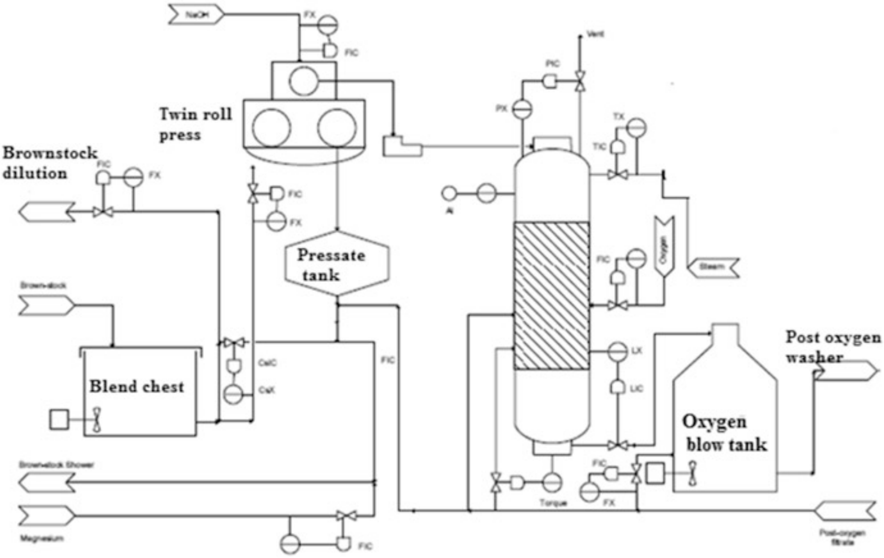


Fig. 4.6 Flowsheet of typical high-consistency oxygen delignification

Fig. 4.7 High consistency oxygen delignification reactor

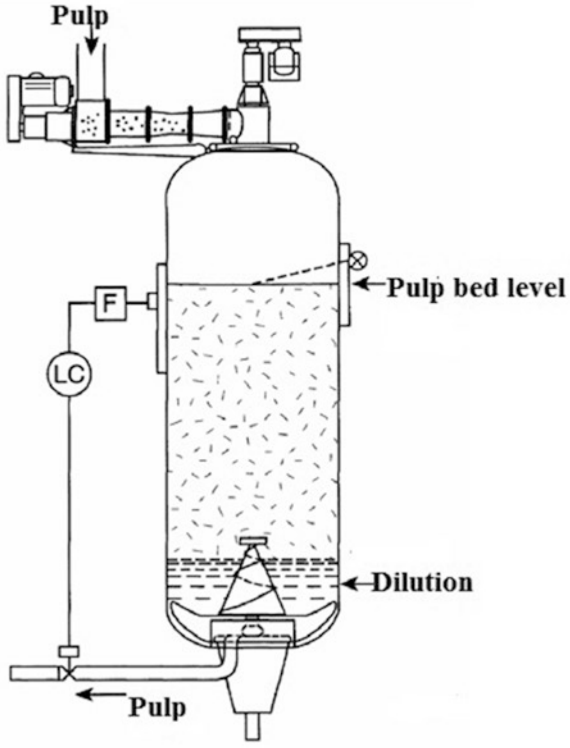


Table 4.6 Typical operating data ranges for oxygen delignification process

Variable	Medium consistency	High consistency
Consistency (%)	10–14	25–30
Alkali consumption (Kg/Tonne)	15–35 (1.5–3.5 %)	15–25 (1.5–2.5 %)
Temperature (°C)	85–105	100–115
Pressure (Bars)	In (7–8);	In (4–6);
	Out (4.5–6.0)	Out (4–6)
Retention time (Minutes)	50–60 (1 Stage);	25–35
	20/60 (2 Stage)	
Oxygen Consumption (Kg/Tonne)	20–24 (2.0–2.4 %)	15–24 (1.5–2.4 %)
Magnesium sulphate (%) (When required)	0–0.02	0–0.02

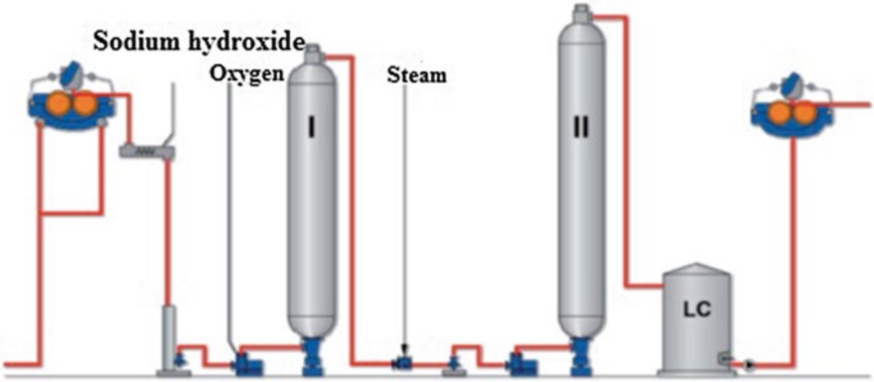


Fig. 4.8 Two-stage oxygen delignification

pressure is used to keep the concentration of dispersed oxygen high. The second reactor operates at lower chemical concentration and pressure but with higher temperature (100 °C) and a longer retention (60 min). Only direct steam to heat the stock is added between the reactors. Other variations on the two-stage oxygen delignification include systems in which washing is carried out between the two oxygen reactors. Studies have shown that interstage washing improves the delignification power of the system (lower kappa out) and reduces the alkali charge required to maintain satisfactory pH levels due to the buffering characteristics of the lignin dissolved in the first stage (Allison and Wrathall 1998). It does not appear that dissolved solids carried over from the first reactor have any adverse impact on the selectivity of the system.

The choice between one-stage and two-stage systems will be dictated by the selected starting kappa number, i.e. the kappa number from cooking, and the selected kappa number from the oxygen stage. The higher the kappa drop in the

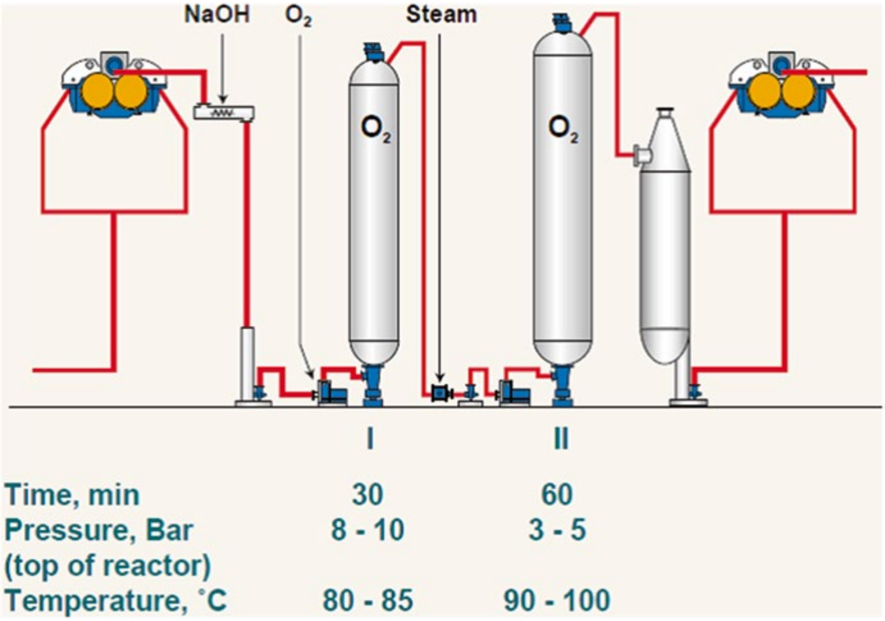


Fig. 4.9 Typical Oxytrac system set up (Alejandro and Saldivia 2003, Reproduced with permission)

oxygen stage, the greater the need for a two-stage system. The kappa number range before the oxygen stage of eucalypt kraft pulp is typically 15–18, while the target kappa number range after the oxygen stage is typically 9–12. While two-stage oxygen delignification is a safer and better choice for softwood due to their higher kappa number at the end of cooking, it is optional for hardwood. Since 1995, the changes to oxygen delignification have been minor and have consisted of changes in process conditions which distinguish the systems provided by the different vendors. The trend towards medium consistency, two-stage installations has strengthened.

In order to maximize pulp yield, the trend is to target a higher digester kappa and a high kappa reduction in the oxygen stage. Most new installations of oxygen delignification favour a medium consistency two-stage process, over a single stage, with or without intermediate washing. Recent improvements in oxygen delignification have been focused on improving the effectiveness and selectivity of the stage (Johnson et al. 2008). For example, the Veracel bleached eucalyptus kraft mill in Brazil is typical of optimal systems that operate the first reactor at lower temperatures (92–96 °C) and higher pressure (6–8 bar) than the second stage (98–100 °C and 3–5 bar).

Oxygen delignification is more selective than most extended delignification processes, but may require significant capital investment to implement (Gullichsen 2000; McDonough 1996; Tench and Harper 1987; Kiviaho 1995). The major benefits of oxygen delignification are decrease of the amount of chemicals, pollution load and the total costs for bleaching chemicals. The chemicals applied to the pulp and the materials removed from the pulp are compatible with the kraft chemical recovery system. This enables the recycling of oxygen- stage effluent to the recovery system by way of the brown stock washers, decreasing the potential environmental impact of the bleach plant. The decrease is roughly proportional to the amount of delignification achieved in the oxygen stage. This applies not only to chlorinated organic by-products, but also to other environmental parameters associated with bleach plant effluents, including BOD, COD, and colour. The decrease in colour, however, is larger than expected on the basis of the lignin removed in the oxygen stage. Oxygen delignification decreases the kappa number prior to chlorination and therefore the effluent load emanating from the bleach plants is reduced.

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

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 oxygen delignification phase in the existing kraft mill may decreases the fibreline production, if there is not enough spare capacity in the whole recovery system. The additional evaporator steam requirements are from 0 to 4 % for 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 with 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 oxygen stage.

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 together.

Table 4.7 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)

Table 4.7 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 highest oxygen delignification while maintaining pulp quality and yield is obtained when the overall delignification-cellulose degradation selectivity is maximized (Van Heiningen and Ji 2012). This is achieved at low alkali concentrations and temperatures of about 100 °C or less. Oxygen pressure has little effect on the selectivity. If the DP of cellulose is optimal, then the pulp yield loss is also minimized because the reduction in cellulose DP is mainly caused by radicals generated by phenolic delignification, and to a much smaller extent by random alkaline hydrolysis. Since the newly generated reducing ends in both cellulose and hemicelluloses undergo peeling reaction, the carbohydrate yield loss is linearly correlated with cellulose degradation. Hexenuronic acids are not removed during optimal oxygen delignification, and must be removed in a subsequent bleaching stage. Although radicals have a negative effect on pulp viscosity and yield, they are also needed for removal of non-lignin and non-HexA oxidizable structures, which contribute to kappa number. This means that for a very high degree of oxygen delignification, the generation of radicals may be essential. In order to increase delignification beyond about 60 % for softwood pulp, the oxygen system design should be changed so that alkali concentration and charge are decoupled, as is similarly done in modern cooking systems, to create a more uniform delignification rate throughout the reactor. 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.

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 burst factor and tear factor at given breaking length. The chemical reactions involved in this process are complex, as the oxygen reacts not only with lignin, but with the other material within the pulp to produce many byproducts and trace elements which can affect the procedure. When higher rates of delignification are required, the two-reactor procedure, which uses differing pressures and temperatures in the separate reactors, is employed. The degree of delignification is dependent upon many separate factors such as pulp consistency, presence/absence of additives/catalysts, pulp initial kappa index, temperature, ambient pH, quantity of alkali and the presence of transitional metals. The greatest single advantage of oxygen delignification is the reduced pollutant output it offers. The technology is compatible with new developments aimed at reducing the discharge of bleach plant effluents. Post-oxygen washing must provide a well washed pulp to the bleach plant to avoid dissolved organic and inorganic carry-over. Post-oxygen washing assumes greater importance as the kappa number is reduced and carry-over becomes a larger component of the bleach plant infeed kappa number. New lines tend to have high efficiency washers such as the drum displacement washers or displacement wash presses as final washing devices.

Investment cost for an oxygen delignification system is typically 35–40 MEuros for 1500 ADt/d bleached pulp production. Its operating costs are 2.5–3.0 MEuro/a. (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 dry solids loads to 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 recausticising and lime kiln. 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 major reason to implement the method. Oxygen delignification is an essential part of any modern, low environmental impact fibreline. Virtually all new fibrelines incorporate oxygen delignification.

4.7 Ozone Bleaching of Chemical Pulps

Significant progress has been made in the use of ozone for emerging green bleaching practice, favouring on-site chemicals production, including complete reuse of byproducts, minimising the ecological footprint and reducing operating costs. Ozone can be used in both chemical and mechanical pulping and has enabled many pulp mills to improve product quality, environmental and process performance (Hostachy and Serfass 2009; Hostachy 2010a, b, c). It is now a state-of-the-art bleaching process; More than 8 million tons per year of chemical pulps are now being bleached with ozone accounting for 8 % of the worldwide bleached chemical pulp capacity. Table 4.8 shows the list of mill using ozone in their bleaching process (Hostachy 2009). Promising growth is also expected in the market segments of dissolving pulps and non-wood fibres. Ozone for pulp bleaching was born at Lenzing in Austria and Union Camp in United States in the 1990s.

Nowadays, ozone is considered as one of the Best Available Technology (BAT) for pulp bleaching. With increasing regulatory pressure and growing market demand

Table 4.8 Mills using ozone bleaching

Mill	Pulp type	Year
Lenzing AG, Lenzing Austria	Birch 1992	1992
IP Franklin (Union C), USA	Mixed hardwood	1992
Kymmene (Wisaforest), Finland	Hardwood/softwood	1993
MoDo Husum Sweden	Hardwood/softwood	1993
Metsä-Botnia Kaskinen, Finland	Softwood	1993
Peterson Säffle, Sweden	Hardwood/softwood	1994
SCA Pulp Sundsvall, Sweden	Hardwood/softwood	1994
Bacell Salvador/Bahia Brazil	Eucalyptus	1995
Sappi Kraft Ngodwana, South Africa	Mixed hardwood	1995
Stora Enso (Consolidated) WI, USA	Hardwood/softwood	1995
Votorantim Jacarei, Brazil	Eucalyptus	1995
Votorantim Luis Antonio Brazil	Eucalyptus	1995
Domtar EB Espanola, Ontario, Canada	Mixed hardwood	1999
Rosenthal Blankenstein, Germany	Hardwood/softwood	1999
Burgo Ardennnes. Belgium	Mixed hardwood	2000
Nippon Paper Yufutsu mill,Japan	Mixed hardwood	2000
OJI Paper Nichinan mill, Japan	Mixed Hardwood	2002
Votorantim,Jaccarei Brazil	Eucalyptus	2002
Nippon Paper Yatsushiro Japan	Mixed hardwood	2003
Lenzing Lenzing Austria	Birch	2003
SCP/Mondi Ruzumberock Slovakia	Hardwood/softwood	2004
OJI Paper, Tomioka Japan	Mixed hardwood	2005
Marusumi Mishima, Japan	Mixed hardwood	2006
Daio Mishima, Japan	Mixed hardwood	2006
SNIACE Cantabria, Spain	Eucalyptus	2007
Paperlinx Maryvale, Australia	Mixed hardwood	2007
ITC Hyderabad, India	Eucalyptus	2008
Celtejo Vila Velha de Rodao, Portugal	Eucalyp/Pine	2008

for better products, the pulp and paper industry faces many challenges and must find new ways to improve environmental and process performance, and reduce operating costs. By choosing ozone in their bleaching process, many pulp mills in various part of the world have already obtained these benefits.

Ozone occupies a very unique position in the whole chemistry involved in Pulp and Paper manufacture. As a gas, produced only from oxygen, and reverting back to oxygen as the final by-product, ozone is an eco-efficient "super oxidant" that needs to be used straight after generation. Ozone can react in seconds to minutes on many of the substances found in pulping and papermaking. The use of ozone has been investigated on many materials such as virgin and recycled fibres, sludge, process waters and wastewaters. Ozone bleaching has already been industrially implemented, experienced and improved from the past 25 years. It is a well proven and safe process, currently used by some reference pulp mills among the most modern in the world. It has advantages in terms of bleaching cost savings, effluent load reduction and usage simplicity. It is applicable to all kind of pulps and has no negative impact on their mechanical properties when the process design is correctly performed. As a result of continuous improvements of the equipment and process automation as well as tuning of the operating conditions for almost 25 years, modern ozone bleaching is recognized today as a state-of-the-art technology for both hardwood and softwood pulps.

Ozone is a powerful oxidizing agent for ligno-cellulosic material (Rice and Netzer 1982). To achieve brightness comparative to chlorine and extraction stages, low lignin pulp from extended pulping or oxygen delignification must be used for ozone bleaching. Ozone is found to efficiently delignify all types of chemical pulps. It is used either at medium or high pulp consistency in ECF and TCF bleaching sequences (van Lierop et al. 1996; Gullichsen 2000; Nelson 1998; Pikka et al. 2000; Lindstrom 2003; Lindstrom et al. 2007; Lindström and Larsson 2003; Vehmaa and Pikka 2007). The typically used charges of ozone are lower than 6–7 kg/t of pulp. As ozone is a very efficient delignifying agent, it can partially or totally replace chlorine dioxide in an economical way (1 kg of ozone replaces about 2 kg of pure chlorine dioxide). The effluent from ozone prebleaching can be used in brown stock counter-current washing and taken to the chemical recovery system, provided its acidic nature is taken into account.

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

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

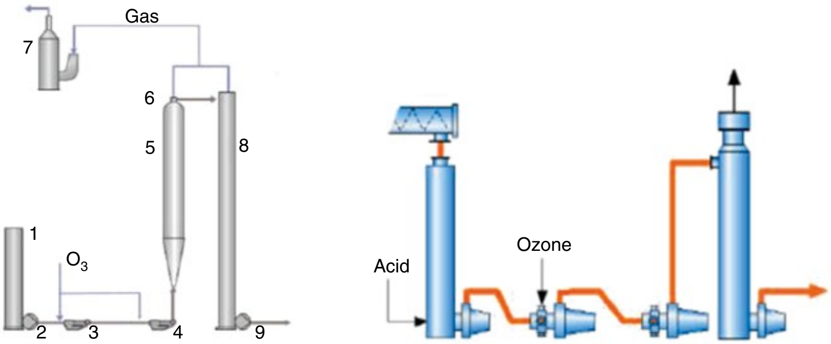
Ozone is manufactured by passing air or oxygen through a corona discharge. The electrical potential used to maintain the discharge is usually in excess of 10,000 V. When oxygen is used, it is possible to produce a mixture of ozone and oxygen containing up to about 14 % of ozone by weight. The manufacture 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 towards lignin than are chlorine and chlorine dioxide and low charges are required to prevent strength loss. Unwanted reactions with cellulose leading to a deterioration in pulp quality occur when large doses are applied (van Lierop et al. 1996). A highly selective ozone treatment remains elusive in spite of the substantial efforts directed towards elucidating the mechanisms of ozone and carbohydrate reactions and the conditions required to minimize these reactions.

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). Since 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 required for ozone generation and also 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 possible to close up the filtrate streams from washing stages. A pressurised (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.

The commercial ozone bleaching installations around the world are operated at medium (about 10 %) and high (about 35–40 %) pulp consistencies, with the majority using medium consistency. Each of these systems has advantages and disadvantages, and there is no general agreement as to which is superior. A higher degree of delignification is obtained in high consistency conditions because a greater charge of ozone (about 0.8 %, pulp basis) can be applied to the pulp. In case of medium consistency, it is difficult to apply more than about 0.5 % ozone (pulp basis). Ozone is used under pressure (0.8–1 MPa) with medium consistency technology to obtain sufficient ozone consumption by the pulp, and mixing is critical. High consistency ozone bleaching uses a gas pressure slightly above atmospheric pressure, and this low pressure minimizes the chance and severity of a gas leak. High pulp consistency involves prior removal of a larger proportion of the liquor in the pulp. The advantage is that there are lower amounts of dissolved organics and heavy metals remaining in the pulp. Medium consistency technology is better suited for a retrofit of a fibreline as existing equipment can be used in many cases. However, the costs for ozone generation and compression in this case are higher (Kappel et al. 1994).

Improvements in medium consistency (MC) ozone bleaching consist in fact of alterations to the ozone mixers. This is no wonder since the ozone mixer is the core of the MC Z-stage and the quality of the final pulp depends on its efficiency. It is worth remembering that the very few mills which faced quality issues are those where the first MC ozone bleaching technique was implemented. This was mainly due to a non homogenous mixing and a mixer which mechanically affected the fibres. Andritz, GL&V and Lenzing Technik are the three suppliers of MC ozone mixers and all MC Z-stages are designed according to the same principles. Industrial practice has shown that Andritz technology requires two mixers in series for a



1. Dropleg
2. MC pump
3. AZ-FS Ozone mixer – 1
4. AZ-FS Ozone mixer – 2
5. Ozone reactor 10-180s
6. Flow discharger with gas removal
7. Scrubber
8. MC blow tube
9. MC-pump

Fig. 4.10 Typical configuration of medium consistency ozone stage (Based on Germer et al. 2011; Vehmaa and Pikka 2007)

3–6 kg/tonne ozone dose to obtain the optimal bleaching efficiency while Lenzing Technik considers that one single mixer of its own is sufficient for a 4–5 kg/tonne ozone charge. Because of the larger amount of filtrate around the fibres at 12 % pulp consistency, the reaction must take place in a pressurized (7–8 bar) reactor and consequently the total gas flow (oxygen and ozone) must be compressed accordingly. In medium consistency systems, the high content of water prevents the effective use of ozone. Figure 4.10 shows typical configuration of medium consistency ozone stage.

The first commercial High consistency (HC) ozone bleaching started in 1992 at the Union Camp mill in Franklin, VA. According to the C-Free® process implemented there, the pulp was pH adjusted, pressed to high consistency, fluffed and transferred to the ozone paddle reactor operating at atmospheric pressure. The C-Free® was provided by Sunds Defibrator until the late 1990s in the United States, Sweden, South Africa and Germany. Modern HC ozone bleaching uses the ZeTracTM technology provided by Metso which is a much simplified version of the C-Free. The experience gained from the first industrial installations showed that ozone requires very short contacting time around 1 min with the pulp and that a 5–10 min extraction stage after the Z-stage is in most cases sufficient. These observations allowed the size of reactors to be reduced, which lowered investment costs. Then the plug screw feeder, the refiner fluffer and the washing stage prior to the extraction stage could all be eliminated. These drastic simplifications led to significant reduction of the capital expenditure, energy requirements, maintenance costs as well as effluent volume. Figure 4.11 shows the principle of the modern ZeTrac

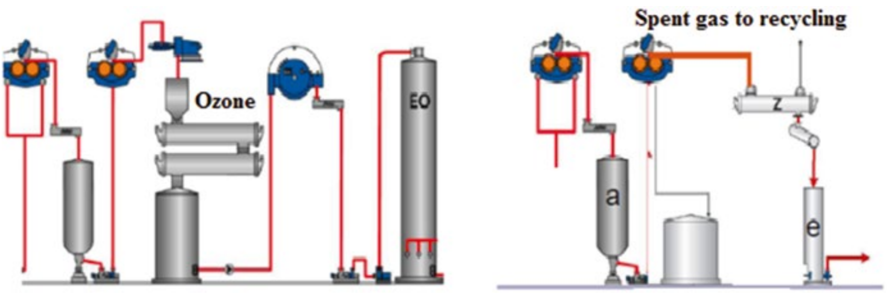


Fig. 4.11 HC Ozone bleaching in 1990s and today (Based on Chirat 2007; Germer et al. 2011)

system. The pulp is acidified and then pressed to high consistency (38–42 %). Such a high consistency is a prerequisite to facilitate the rapid contact between ozone gas and well fluffed pulp and so preserves the reaction efficiency. Once dewatered, the pulp is fluffed in a shredder screw on the top of the press and fed by gravity into the reactor. Ozone is added to the reactor which is operated at a pressure slightly below atmospheric. After the reactor, the pulp is diluted with alkaline liquor (Lindstrom 2003; Lindstrom et al. 2007). In the ozone reactor, the virtually dry fibres whirl around like flakes in a snowstorm allowing the ozone/oxygen mixture to effectively react with the fibres. Another advantage is that in high consistency system the concentration of ozone used can be low, which means lower investment costs in ozone production. ZeTrac enables to build a more closed system with a lower effluent discharge. The system can be closed without mixing acid and alkaline washing filtrates that could lead to troublesome precipitation. Although ozone bleaching is an acidic process, there is no need for washing before alkali is added due to the high pulp consistency. When using ozone in mill operations, the safety aspect is very much important. The ZeTrac process has been designed in such a way that the reactor works at a slight under pressure and thus ensures that no gas can escape to the ambient air. In today's bleaching technology, ZeTrac represents by far the most intelligent way to combine high brightness with care for the environment. The ZeTrac process features the latest development in ozone bleaching technology and the first system was taken into operation at the Burgo Ardennes mill in Belgium. Table 4.9 shows the list of mills using ZeTrac technology. Several ZeTrac projects are under construction in different parts of the world. ZeTrac process allows to combine high brightness and strength with cost efficiency and represents a modern and intelligent way, in which caring for the environment is compatible with quality and production goals.

Depending on the bleaching strategy to be implemented, different bleaching technologies are proposed to mix ozone with the pulp. High consistency ozone bleaching systems represents one of the most efficient solutions. Such high consistency ozone installations have been made for both softwood and hardwood where the ozone charge varies between 2 and 9 kg ozone/adt for the different installations. VCP Jacarei mill in Brazil is using ozone bleaching. In that mill the bleaching

Table 4.9 Mills using ZeTrac technology

IP Franklin, USA
SCA Östrand, Sweden
SENA, Wisconsin Rapids, USA
ZPR Rosenthal, Germany
Burgo Ardennes, Belgium
Oji Nichinan, Japan
VCP Jacarei, Brasil
Ruzomberok1, Slovakia
ITC Bhadrachalam, India

sequence is (Ze)DP. The designed production is 2200 adt/d of bleached eucalyptus pulp and the mill is running up to 2500 adt/d (Carre and Wennerström 2005). The ozone system shows very high efficiency over (Ze) stage since kappa/kg ozone is generally 1.2 with an ozone charge of 5 kg/adt.

Today, when designing a bleach plant for hardwood pulps or eucalyptus pulp, the amount of hexenuronic acids responsible for brightness reversion has to be considered. Ozone bleaching is very effective for removing HexA in a cost-effective way and can be compared to other bleaching alternatives (Wennerström 2002). For example, an ozone bleaching sequence (Ze)DD can be compared with the DHT(OP) DD bleaching sequence including a hot chlorine dioxide stage (DHT), and a reference bleaching sequence D(OP)DD with respect to brightness ceiling and reversion, bleaching chemical cost, mechanical properties and environmental load (Carre and Wennerström 2005). The powerful delignification and brightening capability of ozone allows for a significant reduction of total chlorine dioxide use for an ECF bleach plant, e.g. (OO)(Ze)D, (OO)(Ze)DD or (OO)(Ze)DP, and peroxide in a TCF plant, e.g. (OO)(Zq)P or (OO)ZQ(PO). As an example of that, chlorine dioxide consumption was lowest for the ozone-bleached pulp for reaching a certain brightness and reverted brightness. Furthermore, ozone made it possible to reach higher brightness and reverted brightness targets compared with the reference (Carre and Wennerström 2005). The use of ozone provided the lowest chemical costs for reaching a certain brightness and reverted brightness.

Ozone sequences offer the best options for environmentally sound bleaching. By using ozone in a (Ze)DD ECF sequence, the filtrate from the (Ze) stage can be recovered. The washing after ozone bleaching is alkaline as the ozone treatment is followed directly by an alkaline extraction. This makes it possible to recycle the filtrate after ozone bleaching. This is a unique possibility for the HC ozone system, as the dilution with alkali gives a rapid pH change and thereby precipitation of calcium oxalate is avoided. With presses as washers, the total effluent volume will be 7 m^3/t including 2 m^3/t taken out from the acidification stage ahead of the ozone stage. Comparing the water consumption and effluent load for the light ECF ozone sequence and the DHT bleaching sequence applied on a hardwood pulp, the effluent volume is reduced by 30 % and the COD load by 40 %. As a consequence of the low effluent volume, also the fresh water consumption is low (Carre and Wennerström 2005).

During full bleaching of chemical pulp the last points of brightness are usually difficult to achieve, which is reflected in the relatively high chemical charges needed, and in the rather drastic conditions (temperature and time) required by comparison with those used in the first stages of the bleaching sequence. Moreover, obtaining a constant level of brightness is still an issue in many pulp mills. A new development concerns the use of ozone as a brightening agent applied at the end of a bleaching sequence, where these last points of brightness are usually difficult to gain (Kuligowski et al. 2005; Pipon et al. 2005). One to two kg ozone per ton of pulp is sufficient to produce an instantaneous bleaching effect, increasing the brightness by several points (Pipon et al. 2005). No cellulose degradation takes place under these conditions, and the strength properties of the ozonated pulps are not affected. The process is working equally well at acidic or neutral pH. The efficiency of a last ozone stage depends on the bleaching sequence applied and on the nature of the pulp. In terms of chemical saving, the results obtained in the best cases indicated that 1 kg ozone could replace 2 kg hydrogen peroxide or chlorine dioxide. No cellulose degradation takes place under these conditions, and the strength properties of the ozonated pulps are not affected. The process is working equally well at acidic or neutral pH. The efficiency of a last ozone stage depends on the bleaching sequence applied and on the nature of the pulp.

Different possibilities have been considered to implement ozone as a last bleaching stage. The first consists to transfer ozone into water before mixing the ozonated water to the pulp. The use of dissolved ozone reduces the transfer problems and bleaching occurs in a very short time (few seconds) without any significant ozone loss. However, water quality remains the limiting factor for the process implementation. The best ways to apply ozone consist to use conventional bleaching systems where ozone is introduced into low or medium consistency mixers. Industrial validation of the use of ozone as a last bleaching stage is in progress.

Several studies have been devoted to the increase in pulp yield to improve the overall economy of the production of kraft pulps. Among those, it was demonstrated that by stopping the cooking at a higher kappa number and then applying oxygen delignification, a higher final pulp yield was observed (Kleppe et al. 1972; Jamieson and Fossum 1976; Magnotta et al. 1998). This was explained by the fact that the last phase of a cooking step is less selective than oxygen delignification. Indeed, ozone is a more efficient delignification agent than oxygen. Moreover the presence of a high quantity of lignin protects cellulose from degradation. First experiments have shown promising results which were confirmed on both softwood and hardwood pulps. Chirat et al. (2005) reported that with eucalyptus kraft pulp, ozone treatment applied to the high kappa pulps led to a better overall yield (cooking yield × Z treatment yield) than for the control kraft. For a kappa of 17, the yield gain was 2.3 on wood when applying ozone to the 28 kappa pulp. A better refining ability of the ozonated high kappa pulp was observed and the strength properties were significantly better especially the tear index (Chirat et al. 2005). Applying ozone on high kappa pulps is an attractive way to increase the pulp yield more extensively than the other known alternatives. The high kappa pulps treated by ozone and then fully bleached by an ECF sequence appeared easier to refine than the control kraft pulp, both for softwood and hardwood. Equal or better strength properties than the control pulps were obtained.

In India Metso installed high consistency (HC) ozone bleaching at ITC's Paperboards and Specialty Papers division in Bhadrachalam, India (Sheats 2010). When compared with other technologies, HC ozone bleaching results in lower effluent load and less OX in bleached pulp, lower water consumption, and lower operational costs. ITC is the first company in India to use ozone bleaching (Oinonen 2010). Using ozone has helped to increase the brightness stability and runnability on the paper machine. The pulp mill has a design capacity of 800 tpd blown pulp from Super Batch Cooking Plant. Fibreline one, commissioned in 2002, processes 300 tpd of bleached pulp, while fibreline two, commissioned in 2008, processes 400 tpd of bleached pulp. Fibreline one was originally built with ECF sequence of Do-EOP-D1, but was retrofitted with ozone bleaching in 2008, while fibreline two has a bleaching sequence of Ze-DP. Technically, the production of ozone is by electric discharge of oxygen rich feed gas using a special generator and the generator at ITC has a capacity to produce 200 kg/h ozone at 12 % concentration and can reach up to 230 kg/h at 10 % concentration. Parameters that affect the bleaching process include consistency, temperature, pH and retention time. The ozone bleaching technology has provided reduction in chlorine dioxide and hydrogen peroxide consumption, together with better pulp quality, improved strength properties and reduction in AOX generation (Sharma 2010). This technology is technically, environmentally and commercially superior to conventional ECF technology and that the runnability of paper machines improves with ozone bleached pulp.

The Oji Paper Co Ltd's Nichinan Mill, Japan has moved to ECF operation using a Ze-Trac system from Metso Paper introduced into the Z stage for the first time in Japan. Operating experience has highlighted the four most important areas in ozone reaction efficiency: pulp pH; pulp consistency; gas flow in the ozone reactor; and pulp retention in the ozone reactor. Following optimisation of these four parameters, pulp strength as measured by burst index and tear index were unchanged, except for slightly lower viscosity. There was no effect on machine runnability. The cost of ozone ECF bleaching is particularly sensitive to the price of electricity. This is of particular significance in Japan, where electricity costs are particularly high. Discharges of adsorbable organic halogen AOX and COD have fallen and hypohalite (OX) in bleached pulp has been reduced by approximately 30 %.

At Ruzomberok, Slovakia, an existing D(EOP)DED bleaching sequence with two alkaline extraction (E) stages was converted to HC ozone bleaching, with a resulting bleaching sequence of Z(EO)(DnD). The results obtained at the Ruzomberok mill with Metso's ZeTrac HC ozone bleaching process showed only minor differences in pulp properties before and after the installation of ozone bleaching, and the effluent load and organic chloride compounds were significantly reduced.

For a while many mills looked at ozone bleaching to produce TCF pulps because of tightening environmental regulations. Today ozone is seen as a complement to produce ECF at a lower cost than standard ECF pulp without ozone. With replacement ratios of chlorine dioxide by ozone in the range of 2.0–3.5, savings of 6–8 US$/mT of pulp net can be achieved. Whenever chlorine bleaching chemicals are replaced by non-chlorine chemicals, a reduction in AOX is seen. When ozone completely substitutes the first chlorination stage (C/D), then the extract from the washers following the ozone stage can be recycled to the chemical recovery system leading them closer to closing the mill water loop. If an extraction stage follows the ozone stage, the extract from this washer can also be recycled. This is greatly desired since most of the COD and BOD, are contained in this extract.

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

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

Bleaching plants that do not yet have oxygen delignification can achieve AOX levels of the order of 0.3 kg/tonne pulp after effluent treatment by combining "wise man's" delignification with D/Z-based ECF bleaching. The cost of such sequences, capital charges for process equipment included, is comparable or lower than that of standard ECF solutions whose AOX levels are nearly twice as high. By adopting D/Z-based bleaching, the mill will be in a position to gradually upgrade its sequence to meet evolving effluent standards or market demands, while minimizing the risks of making soon-obsolete investments. Whether it concerns greenfield mills, new bleach lines or retrofit projects, whether the mill wishes to adopt ECF or TCF sequences, oxygen and ozone are today the most cost effective bleaching chemicals available to the Pulp and Paper Industry. Investment costs for a 1500 Adt/d ozone bleaching system are 12–15 MEuro. Corresponding operating costs are 1.8–2.1 MEuro/a (European Commission 2001). The reduction of AOX emission to water is the main reason to use this technology.

4.8 Ozone for High Yield Pulping

Continuous investigation has brought major gains in the mechanical pulping industry regarding reduction of the energy consumption and improvement of pulp and paper quality. However, a more energy efficient pulping process producing better quality pulp and paper is always the major focus for maintaining competitiveness inspite of the continuous increase of manufacturing costs, including fibrous materials and energy costs. For mechanical pulp fibres, one of the main reasons for low inter-fibre bonding is the presence of lignin, although the hydrophobic lignin needs to be retained to give the high yield and high bulk property to mechanical pulp (Li et al. 2010). Using a chemical agent to modify the lignin-rich material on the fibre surface can improve the bonding ability of mechanical pulp fibres while preserving the high yield. Ozone is known to be a powerful oxidizing agent that has already been used in industrial pulp bleaching (Germer et al. 2011; Cloutier et al. 2009; Cloutier et al. 2010). It has a positive effect on both energy savings (Lecourt et al. 2007; Petit-Conil 2003) and on pulp qualities (Katz and Scallan 1983). Several practical studies have been conducted on the use of ozone during high yield pulping. Ozone was initially investigated on thermo-mechanical pulp (TMP) collected from the main or reject line to reduce energy requirement and to improve pulp strength properties (Allison 1979, 1980; Soteland 1977, 1982; Lindholm 1977a, b).

Ozone was used for the first time in a mechanical pulping process in 1964 (Ruffini 1966). It was mainly applied on SGW, RMP or TMP pulps after secondary refining to increase pulp strength properties. The efficiency could be classified as such: TMP>RMP>SGW. It was also studied between defibering and refining stages of TMP or CTMP processes in order to reduce energy consumption and to improve the pulp quality (Allison 1979; de Choudens and Monzie 1978; Eriksson and Sjöström 1968; Lindholm 1977a, b, c; Lindholm and Gummerus 1983; Soteland and Loras 1974; Vasudevan et al. 1987).

During pulp refining, ozone plays the role of a “chemical” refining agent complementing mechanical energy normally provided by refiners. The softening action of ozone facilitates fibre separation. During the last decade, efforts were made to clarify the remaining limitations to achieve the full-scale implementation (Hostachy 2010a, b, c). The main points were the identification of the best application point to maximize energy reduction and the build-up of the full scale mixing equipment regarding practical aspects (mixing, safety etc.). In a thermo-mechanical process in order to achieve the same final freeness, about 0.65 MWh per ton of pulp can be saved using 20 kg/t ozone on both Spruce or Pine TMP pulps. The net saving is about 0.4 MWh per ton of pulp, considering energy for oxygen and ozone production (Soteland and Loras 1974; Lindholm 1977a, b, c). In case of softwood species, decrease in brightness was observed whereas the inverse was observed for hardwood species. This showed that the lignin structure was an important parameter in ozone reaction. The energy consumption reduced by 45 %, the tensile and tear properties increased by about 90 % when a charge of 2.5 % in ozone was applied on birch primary-refined CTMP in alkaline medium as an interstage (Soteland 1982).

However, brightness and pulp yield reduced by three points. Oxidation of lignin by ozone modified the fibre surface (Kojima et al. 1988; Kojima and Yoon 1991). Petit-Conil et al. (1998) conducted detailed study on the effect of inter-stage ozone treatment. Up to 40 % energy saving was achieved for an ozone charge of 3 %, and pulp quality improved with softwoods and hardwoods without adverse effect on brightness and pulp bleachability. Ozone reacted with fibre wall components at the fibre surface (Kibblewhite et al. 1980; Rothenberg et al. 1981). Ozone reacted with lignin by oxidizing the lateral chains associated with a depolymerisation of the macromolecule, by opening the aromatic ring and by forming water-soluble organic acids. This delignification occurred in the composite lamella modifying the fibre flexibility. With polysaccharides, an oxidation of terminal hemiacetal groups was found to produce some aldonic acids. The oxidation of primary and secondary alcohol groups produced some carbonyl and carboxyl groups by opening the pyranosidic ring. In case of mechanical pulps, the hemicelluloses were found to be affected and the cellulose was generally protected by the lignin (Magara et al. 1998). All these chemical reactions modified the hydrophilicity of the fibre surface. This increased the interfibre bonding potential. Also, ozone could act as a chemical refining agent. It was found to increase fibre wall hydration and facilitated microfibril separation. This resulted in a decrease in pulp freeness after ozonation (Petit-Conil 1995; Petit-Conil et al. 1997; Petit-Conil and de Choudens 1994). The lignin of ozonated softwood TMP was analysed by 13C NMR (Robert et al. 1999). The carbon skeleton presented far fewer structural modifications than the lignin extracted from the chemical pulps. No correlation was observed between the strength improvement and the increase in carbonyl groups in lignin. Ozone did not degrade the polymeric structure of lignin in mechanical pulp. The improvement in pulp strength properties was explained by the increase in fibre flexibility. Ozone was an efficient bleaching agent for TMP if charges between 0.1 and 1 % were used (Hsieh et al. 2000). Saharinen and Nurminen (2001) reported that bulk and the internal cohesion of multilayer board can be enhanced by ozonating mechanical pulp. A charge of ozone lower than 3 % at low consistency increased the Scott bond of long fibres by 250 % without decrease in bulk.

Ozone has been found to be a selective agent for removing resin and fatty acids in CTMP effluents (Roy-Arcand and Archibald 1996). Small charges of ozone are found to be sufficient for degrading these harmful components in effluents and reducing effluent toxicity. Now a days, mechanical pulp producers are faced with a significant increase in energy costs. Even if ozone production consumes electricity, its application in the process is an alternative to be considered not only to decrease specific energy but also to improve pulp quality, pulp bleachability, runnability on the paper machine and the pulping effluent.

Lecourt et al. (2007) investigated ozone in the main line (directly in refiners) or in the reject line to reduce energy consumption in TMP pulping. The experiments were conducted with spruce chips at pilot plant scale (ozone in refiners) and at laboratory scale (reject treatment). The use of ozone in primary or secondary refiners modified the fibre separation mechanisms and reduced electrical energy consumption by 10–20 %. Ozone was shown to mainly oxidise the wood extractives and consequently modified the fibre surface chemistry and the final pulp quality. Ozone treatment of TMP rejects appears a very promising technology. An ozone charge of 1–2 % saved energy by 10–20 %. It also resulted in degradation of wood extractives and modification of lignin at the fibre surface. The reintroduction of these ozonated-refined reject fibres in the TMP accepts improved the strength properties and the peroxide bleachability of the final pulp. These effects could quite easily compensate the costs of ozone generation and use.

Sun et al. (2013), found that the presence of sodium hydroxide is important in the ozone treatment of mechanical pulp. Ozone has a good performance when the reaction pH is between 5.4 and 6.15 and the reaction is carried out with whole primary pulp. Short fibres and fines have much larger specific surfaces and more contact with chemical components than do long fibres (Han et al. 2008). The effect of selective refining of the primary long-fibre fraction combined with an inter-stage ozone treatment on energy consumption and pulp qualities has been recently studied (Sun et al. 2014a, b). Secondary pulp was recombined with the primary short-fibre fraction to form the initial pulp for comparison with a traditional TMP process. Selective refining shows a significant advantage with respect to refining energy. About 15 % total refining energy could be saved when obtaining a pulp of 100 mL freeness, compared with the control TMP trial. With use of 1.5 % ozone, another 13.8 % energy savings can be achieved. Selective refining does not greatly change the physical properties of the handsheet, and an increase of the light scattering coefficient can be observed. Treatment of primary long fibres with ozone can modify the secondary pulp properties compared with selective refining only. But, this improvement could disappear when secondary pulp is recombined with primary short fibres. This is mainly due to the poor bonding ability of the primary fines. For the optical properties, the same phenomenon does not exist. Recombination of long fibres and fines results in an augmentation of the handsheet brightness, opacity and light scattering coefficient.

Concerning the use of ozone in high pulping processes, a promising field of new applications is just opening. Sustainability in raw material supply and better control of energy requirement are of major interest for many pulp and paper companies.

4.9 Elemental Chlorine-Free Bleaching (ECF) Bleaching

The realization that chlorine-based pulp bleaching sequences exhibited a significant and potentially negative impact on the environment, and the promulgation of the “Cluster Rules” in the United States (USEPA 1997) and similar regulations in several other countries led to a virtual explosion of research examining alternative bleaching chemistries during the late 1980s and early 1990s (Department of Justice 2012; Environment Canada 1992a, b; Rajotte 2000; Shrinath and Bowen 1993). Several alternative chemicals – peroxide, peroxyacetic acid, peroxyformic acid, potassium peroxymonosulfate (Oxone), dimethyldioxirane (which is generated in situ from acetone and potassium peroxymonosulfate), peroxymono-phosphoric acid, various enzymes, polyoxomolybdates, Monox-L, dithionite, ozone, chlorine dioxide, and oxygen have been investigated (Brogdon and Hart 2012; Ragauskas et al. 1993; Bouchard et al. 1996; Springer 1997; Harazono et al. 1996; Katsoulis 2002;. Heimburger et al. 2002; Yant, and Hurst 1991; Carreira et al. 2012; Peter 1993; Nutt et al. 1993; Gotlieb et al. 1994; Helander et al. 1994; Homer et al. 1996; Reeve 1996; Rapson and Anderson 1978; Ni et al. 1992; Berry 1996; Parthasarathy 1997). Research into the formation of adsorbable organic halogens (AOX), chloroform, and other bleach plant pollutants showed that higher kappa number pulps entering the bleach plant tended to increase the amount of these pollutants being formed (Dallons et al. 1990; Knutson et al. 1992). As a result of these findings, a significant amount of research effort was expended on developing methods that could be used to reduce the kappa number of pulp entering the bleach plant. Some of these efforts included cooking modifications to extend delignification in the digesters (Jameel et al. 1995; Sezgi et al. 1994; Walkush, and Gustafson 2002; Buchert et al. 2001; Goyal et al. 1994). Other methods of lowering the entering kappa number included the use of oxygen bleaching (Carter et al. 1997; Croon and Andrews 1971) and enhancements to oxygen delignification, including pretreatment with nitrogen dioxide (Prenox) (Brännland et al. 1990) and the use of nitrosyl sulfuric acid (NSA) (Ku et al. 1992). By the end of the 1990s, commercial bleaching sequences had evolved to virtually eliminate chlorine and hypochlorite as viable bleaching chemistries (Reeve 1996). Most of the kraft pulp industry had now settled on ECF bleaching as the sequence of choice (Pryke et al. 1995, 1997, 2003; Govers et al. 1995; Moldenius 1995, 1997). ECF bleaching sequences tend to use chlorine dioxide, caustic, oxygen, and peroxide as the main bleaching chemistries (AET 2008b).

The science, a proven environmental track record, and strong market demand demonstrate that ECF is without rival in terms of pollution prevention, resource conservation, and product quality. According to Dr. Robert Huggett, former United States. EPA Assistant Administrator, Research & Development “Chlorine dioxide is a solution to dioxin and other persistent, bio-accumulative, toxic substances in mill waste water” and according to Professor Don Mackay, former member of the International Joint Commission, the Great Lakes Science Advisory Board and its Virtual Elimination Task Force “ECF is an excellent example of enlightened industrial response to an environmental concern and should be embraced by the environmental community”. ECF technology is the ‘best available technology’ selected for the paper grade kraft mills.

ECF pulp, bleached with chlorine dioxide, continues to grow and now dominates the world-bleached chemical pulp market (Pryke 2003; AET 2002a, 2007, 2008a, b, 2013). ECF pulp, bleached with chlorine dioxide, continues to dominate the world bleached chemical pulp market. In 2012, ECF pulp production reached ~94 million tonnes, totaling more than 93 % of world market share (Table 4.10). Totally Chlorine-Free (TCF) production declined modestly, while sustaining a small niche market at less than 5 % of world bleached chemical pulp production. Moreover, since the market downturn in 2008 and 2009, ECF pulp production has rebounded both with restarts of previously idled production and new greenfield pulp mills.

Table 4.10 World bleached chemical pulp production: 1990–2012

	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
2010	88.3	4.8	2.4
2012	93.9	4.7	2.4

In Scandinavia, ECF accounts for over 80 % of bleached chemical pulp production. 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 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 United States production came into compliance with the United States Environmental Protection Agency's 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 declined by approximately 4 million tonnes over the period 2005–2010. However, since then, a number of idled bleached mills restarted, adding back approximately 1.6 million tonnes to North American ECF pulp production. Moreover, an additional 0.5 million tonnes are expected to restart in 2014. In South America, ECF production continues to grow rapidly. An additional 2 million tonnes of new ECF production was added in the region since 2010. In 2012 ECF represented over 97 % of bleached chemical pulp production. Production of ECF pulp is also growing in the South East Asia region (AET 2013). Significant ECF capacity was added in Indonesia and China in the recent years.

In China where small mills are being shutdown, 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 (AET 2007).

Over the next five years, bleached chemical pulp production is set to increase dramatically with significant expansions and new investments totaling more than 13 million tonnes planned for China, Uruguay, and Brazil. All of this new production is expected to be ECF. ECF's market share will continue to grow due to it's acknowledged environmental compatibility, cost-competitiveness, and high quality desired by producers and users alike.

Different kinds of ECF bleaching processes have been reported. Traditional ECF processes replace elemental chlorine with chlorine dioxide. Enhanced ECF processes use oxygen delignification and/or extended delignification to remove more lignin during the pulping process before bleaching the pulp with an ECF process. Low-effluent ECF processes have modified an enhanced ECF process to send additional organic waste generated in the bleach plant back to the chemical recovery system. In a low-effluent ozone ECF process, ozone replaces chlorine dioxide in the first bleaching stage of an enhanced ECF process. A second approach uses an enhanced ECF process but installs additional technologies in other parts of the mill to remove chlorides from the bleach plant filtrates.

Examples of typical modern ECF bleaching sequences are shown in Table 4.11. Sequences including only D and E stages are called "straight ECF" whereas those including D in combination with P and (PO) are called "ECF light" and "ECF super light" (Bergnor-Gidnert 2006). These sequences are also sometimes called "low-impact ECF", "low-AOX ECF" (e.g. Aracruz Barrado Riacho, Brazil) and "low-OX ECF" (e.g. Line C at Votorantim Celulose e Papel Jacareí, Brazil.

Generally, to reach a certain brightness target, hardwood requires fewer chemicals than softwood, which usually means that the number of bleaching stages can be shorter. Over the years, the use of chlorine dioxide has substantially decreased in bleaching and has been replaced by oxygen based chemicals. ECF light and ECF super light sequences can be applied for both hardwood and softwood, depending on the brightness target (UNEP 2006).

Recent studies comparing ECF and TCF have reiterated ECF's overwhelming product and yield advantages and ECF's environmental compatibility with aquatic ecosystems (Beca AMEC 2006). 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 nonchlorine bleaching concepts, including TCF. These investigations have reached a common conclusion (Hamm and Gottshing 2002; Tana and

Table 4.11 Modern ECF bleaching sequences

O/ODEDP
O/OADPZP
O/OADED
O(OPDQ(PO)
O/ODED
O/OZEDD
OQ(PO)(DQ)(PO)
O/O(Q)OP(Paa/Q)PO
O/ODEDD
OQXOP/ODEPDPaa
O/OADEDP
O/OZDP
O/O(Q)OPDPO

A Acid wash to remove metal element from pulp, *D* Chlorine dioxide, *E* Alkaline extraction, *EO* Alkali extraction reinforced with oxygen, *EP* Alkali extraction reinforced with hydrogen peroxide, *EOP* Alkali extraction reinforced with oxygen and hydrogen peroxide, *mP* Modified peroxide, *O* Oxygen, *P* Peroxide hydrogen peroxide (H_2O_2), *Paa* Peracetic acid, *Q* Chelating agent, *X* Xylanase, *Z* Ozone, *ZD* Ozone and chlorine dioxide added sequentially in same stage

Lehtinen 1996). Studies comparing ECF and TCF effluents confirmed the absence of significant differences in biological effects in the aquatic environment.

ECF bleaching is practiced on both conventional and reduced kappa pulps (Chirat and Lachenal 1997). Few examples of commonly used ECF bleaching sequences are OD(EOP)D, D(EO)DD, D(EOP)D, AD(EO)DOD (EO)DD, O(AD)(EOP)D, (EOP)D(PO)D (Pikka et al. 2000). The oxygen delignification stage can include one or two stages. An acid hydrolysis stage is especially suitable for hardwood pulps. Chemical consumption varies with wood species and mill and is especially connected to kappa number. The chemical consumption (kg/ADT) of a mill using D(EO)DD bleaching of oxygen-delignified softwood pulp from kappa number 12–90 % ISO brightness are: chlorine dioxide (as equivalent chlorine), 44; sodium hydroxide, 15; oxygen, 4; and sulphur dioxide, 1.5. Another typical ECF bleaching sequence is D(EOP)D(ED). The first D stage has a retention time of less than 1 h and a temperature of about 60 °C. The alkaline stage is preferably pressurized, and oxygen and hydrogen peroxide are added to boost the delignification in this stage to reduce subsequent chlorine dioxide consumption. The two final D stages normally have a retention time of 3 h each, and the temperature is 70–75 °C. Diffusers on top of the chlorine dioxide bleaching towers do the washing after each stage. Wash press is generally used after the EOP stage. The wash press in this position gives a higher degree of flexibility for filtrate circulations and reduction

Table 4.12 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 No. 12

of effluent volumes. Table 4.12 shows typical mill data in case of DEOPDED sequence with softwood Kraft pulp of 12 kappa number. Brightness vs. consumption of active chlorine for pulps bleached in three, four and five bleaching stages is presented in Table 4.13. In this example, the three-stage sequence can reach a brightness target of 88 % ISO. The four-stage sequence can go upto 90 % ISO and the five-stage sequence upto 92 % ISO.

Besides the number of bleaching stages, the amount of bleaching chemical added to the first stage (the kappa factor) also affects the brightness development. Introduction of an ozone stage in a chlorine dioxide bleaching sequence means that the consumption of chlorine dioxide required to reach a certain brightness can be reduced considerably. Table 4.14 shows brightness vs. active chlorine charge for the sequences D(EOP)DD and Z(EO)D(ED). In the ozone sequence, filtrate from the prebleaching Z(EO) treatment can be used as wash water in oxygen delignification washing. Replacing the last (ED) stage of a chlorine dioxide bleaching sequence with a pressurized peroxide stage reduces the need for chlorine dioxide. The effect of peroxide use in a chlorine dioxide bleaching sequence is presented in Table 4.15. Chlorine dioxide demand can also be reduced by using ozone synergistically with chlorine dioxide.

Table 4.16 shows the bleaching sequences implemented in the latest designs of eucalyptus-based pulp mills.

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 which are listed below:

- 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
- 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 % hydrogen dioxide, 30 % consistency and 4 h at 90 °C) (Desprez et al. 1993). A similar, forcing, final peroxide stage can allow full bleaching of softwood kraft pulp in the OQPDP sequence (Q – chelation stage) (Devenyns et al. 1993). This is one step further along the road to TCF bleaching than the

Table 4.13 Brightness development in different chlorine dioxide bleaching sequences

Chemical consumption (kg act Cl/odt)	Brightness (% ISO)		
	D(EO)DED	D(EO)DD	D(EO)D
20	81.0	–	
30	89.0	87.0	86.0
40	91.0	89.5	88.0
50	92.0	90.0	–

Based on data from Pikka et al. (2000)

Table 4.14 Brightness development in a sequence replacing the first D-stage with a Z-stage

Kg active Cl/ton	Brightness, % ISO	
	D(EOP)DD	Z(EO)DnD
15	87.0	–
20	89.2	–
27	90.0	–
35	–	84.2
40	–	86.2
47	–	88.5
52	–	89.2

O_2 delignified pulp, Kappa No. 11.1
Based on data from Pikka et al. (2000)

Table 4.15 Effect of peroxide use in a chlorine dioxide bleaching sequence

Chlorine dioxide consumption (kg act Cl/ADMT)	D(EOP)D(PO)		D(EOP)D(ED)
	Cons. in PO stage (5.5 kg)	Cons. in PO stage (3.0 kg)	
36	91.0	91.9	–
41	–	–	90.2
53	–	–	90.5
64	–	–	90.6

Lab ITC™, O_2 delignified pulp; Kappa No. 12.0; Viscosity 1017 dm^3/kg
Based on data from Pikka et al. (2000)

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 1995, 1997). Mill studies in Canada and the United States have shown high brightness, 89–90 % ISO and high strength (burst, tear, tensile and viscosity) pulps are produced with ECF (Pryke et al. 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.

Table 4.16 Modern bleaching sequences of eucalyptus-based kraft pulp mills

Eucalyptus-based kraft pulp mills	Bleaching sequence
VERACEL	AD0 EOP D1 P
ARACRUZ C	AD0 EOP D1 D2
RIPASA	Dhot PO D1
UPM FRAY BENTOS	AD EOP D P
ENCE-NAVIA	D0 EOP D1
VALDIVIA ARAUCO	D0 EOP D1 D2
NUEVA ALDEA	Dhot EOP D1 D2
SANTA FE CMPC	AD0 EOP D1 D2

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
- Bleaching cost increased modestly by 5–10 %.

ECF is integral to achieving the vision of minimum impact (Haller 1996; Axegård et al. 2003; European Commission 2001; Pryke 2003). Pulping and bleaching strategies incorporating ECF produce strong softwood fibres, minimizing the reinforcing fibre requirements for many paper grades such as lightweight coated (LWC). It has also been recognized that in combination with enhanced pulping, ECF manufacturing has a higher yield, using the least amount of wood compared with other pulping and bleaching techniques. Finally, ECF is compatible with, and at the leading edge of, so-called 'closed-loop' strategies for minimizing wastewater from bleaching (Pryke 2003). Along with efficient wastewater treatment, closed-loop strategies are providing optimal solutions for protecting and sustaining the receiving water ecosystem (Stratton and Gleadow 2003; Anonymous 1997).

During the 1990s, governments, responding to the environmental concerns posed by persistent, bio-accumulative, and toxic compounds, developed new regulations for their respective pulp and paper industries. A common feature of many of these regulations and guidelines is the concept of 'best available technology' (BAT). Recognizing excellent performance, the United States 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 Environmental Protection Agency predicts that over time all remaining dioxin advisories downstream of mills in United States should be lifted following conversion to ECF bleaching. Conversion of existing mill to ECF mill has been possible but require often considerable modifications in the fibreline 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.

4.9.1 Modified ECF Sequences

One promising trend today is the use of modified ECF sequences, i.e., sequences which still use chlorine dioxide, but not in the traditional manner of DEDED or ODED sequences (Chirat and Lachenal 1997). The key here is to make them as efficient as chlorine-containing sequences (Andrew et al. 2008). The use of chlorine dioxide and ozone in combination – in (DZ) or (ZD) stages—has started to appear in the recent years. Indeed, basic chemistry tells us that the reactions of these two chemicals on lignin complement each other, for example as with the case of chlorine and chlorine dioxide combinations (DC). It makes the process more efficient than DO or Z alone. The other interest in combining the use of ozone and chlorine dioxide lies in the fact that the required operating conditions (temperature, pH) are similar for the two chemicals, making it possible to run (DZ) or (ZD) stages with no intermediate washing. The criterion in the process is the replacement ratio, i.e. the amount of chlorine dioxide replaced by 1.0 kg of ozone. Ozone and chlorine dioxide (as pure chlorine dioxide) being of the same order of cost today, a replacement ratio higher than one means a reduction in chemical cost.

Table 4.17 shows an example of the (ZD) and (DZ) processes applied to a softwood kraft pulp. This type of combination has been thoroughly studied in France, both in the laboratory and at pilot scale to optimize the process. The (ZD) process is already in use in a few mills and several other projects announced recently intend to utilize it. This process provides a good example of how a relatively simple retrofit in an existing mill can meet most of the requirements described earlier.

ECF bleaching eliminates 2,3,7,8-TCDD and 2,3,7,8-TCDF to non-detectable levels. However, the complete elimination of dioxins in ECF bleached effluents is a question of kappa-number and purity of chlorine dioxide. With high kappa and impure chlorine dioxide (i.e. high concentration of chlorine) the probability of forming dioxins increase. ECF bleaching eliminates the priority chlorophenols proposed by the United States Environmental Protection Agency (EPA) for regulation to non-detectable 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 <0.3 kg AOX/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 which require considerable amounts

Table 4.17 (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 (kgClO_2/kg.O_3)	–	20.1	1.7
AOX (kg/ODT of pulp)	1.5	0.65	0.61

AOX measured on the combined effluent

Based on data from Chirat and Lachenal (1997)

[a] Kappa number 24

of energy in manufacturing of chlorine dioxide, oxygen and hydrogen peroxide. The production of ECF has been tested and practised in full-scale pulp lines for several years.

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.

In the United States, the ECF process is regarded as BAT and in Europe, the Commission has decided that there is no significant difference between TCF and ECF and, therefore, both are regarded as BAT. Tables 4.18 and 4.19 show environmental aspects of ECF and TCF bleaching processes.

In the last decades the ECF technology has developed remarkably, and the modern ECF bleaching provides pulp with same or even lower environmental impacts than TCF. ECF bleaching, in combination with oxygen delignification, provides – with lower energy consumption – higher yield and produces stronger fibres compared to TCF bleaching. This, in turn, enhances the ability to recycle the products made out of the pulp and contributes to more efficient use of wood resources. ECF pulp also has higher brightness than TCF pulp. Studies by the International joint Commission, the European Commission, the Darmstadt Technical Institute for Papermaking in Germany and documented reports from industry sources support the efficacy of ECF. The modern ECF pulp mills use bio-activated sludge in wastewater treatment, so the water released back to the watercourses is virtually free of toxic substances.

ECF manufacturing produces the strongest fibres, while conserving forest resources and enhancing recyclability. In combination with enhanced pulping strategies, ECF manufacturing has a higher yield, using the least amount of wood compared to other

Table 4.18 Environmental aspects of ECF and TCF – effluent quality

	ECF	TCF
AOX (adsorbable organic halides)	Some AOX content from bleaching process but substances are different to those produced by chlorine gas and are non persistent. Modern effluent plants reduce this content to a level which is insignificant	none
Molecular weight of compounds in effluent	Generally high molecular weight (and therefore less toxic) compounds detected	Low molecular weight compounds such as glyoxal and vanillin
Short-term single species toxicity	TCF and ECF equal	TCF and ECF equal
Chronic single species toxicity	Slightly lower and below toxicity level of natural peat bog water and municipal effluent	Slightly lower and below toxicity level of natural peat bog water and municipal effluent
Overall environmental watercourse impact	TCF and ECF equal and below toxicity level of natural peat bog water and municipal effluent	TCF and ECF equal and below toxicity level of natural peat bog water and municipal effluent
Results of biological tests on effluent of mills having both TCF and ECF plants	TCF and ECF equal	TCF and ECF equal
Endocrine disruption	There is some evidence of endocrine disrupting substances in the effluent of both processes but these are believed to originate from wood or naturally-occurring chemicals and the impact from the two processes is indistinguishable	

Table 4.19 Environmental Aspects of ECF – Pulp properties

Brightness	Bleaching reduces pulp strength. At the same level of reduction, ECF produces pulp having approximately 2 ISO points brighter than TCF
Yield (i.e.) how much pulp can be made from the trees	For hardwoods, ECF has an approx. 2 % higher yield than TCF and for softwood, this advantage rises to around 4 %

bleaching processes. And finally, ECF is compatible with, and at the leading edge of, closed loop strategies for minimizing wastewater from bleaching. Along with efficient wastewater treatment, closed loop strategies are providing optimal solutions for protecting and sustaining the receiving water ecosystem.

The measure can be adopted in new and existing kraft mills. Conversion of existing mill to ECF mill has been possible but require often considerable modifications in the fibreline 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.

The investment costs for a 1500 ADt/d ECF bleaching system are 8–10 MEuros at new mills and 3–5 MEuros at existing mills. The operating costs are 10–12 MEuro/a (European Commission 2001). 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 world's papermakers desire for ECF's superior product quality remains unabated. With such strong attributes, new bleached chemical production will come to the market using ECF based bleaching technology. The future remains bright for ECP pulp production.

4.10 Totally Chlorine-Free (TCF) Bleaching

Bleaching sequences that use no chlorine chemicals are termed as TCF. TCF is the culmination of several technologies involving oxygen, ozone, hydrogen peroxide, and various other peroxygens.

TCF bleaching processes significantly reduce the effluent loadings and allow total closure. TCF bleaching began to be practiced on a commercial scale basis in the paper industry beginning in the late 1980s. However, developments leading up to the various TCF technologies began much earlier in the twentieth century.

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. Examples for different TCF bleaching sequences are listed in Table 4.20 (European Commission 2013). 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 fibrelines that also bleach pulp with the use of chlorine chemicals. Typical chemical consumption (kg/ADT) in oxygen chemical bleaching of softwood kraft pulp of kappa number 10–88 % ISO brightness are: hydrogen peroxide, 20; sodium hydroxide 32; oxygen, 6; ozone, 5; sulphuric acid 20; and EDTA, 2. Peroxide and oxygen are not sufficient to delignify the pulp further when the kappa number of the pulps is low. Ozone or peracids are more efficient delignifying chemicals, and can be used to reduce the kappa number to a low level before the final brightness increase in the pressurized peroxide stage. Chemical consumption for bleaching softwood kraft pulp of kappa number 11–89 % ISO brightness in Q(OP)(ZQ)(PO) sequence is shown in Table 4.21. The chemical charges and process conditions will obviously vary depending on wood species, degree of system closure, etc. The brightness development in TCF sequence depends on the proportions of various chemicals used. Table 4.22 compares the sequences (QZ)Q(PO), QpaaQ(PO), and Q(PO) for a Scandinavian softwood kraft pulp of

Table 4.20 Bleaching sequences for TCF bleaching

Softwood kraft pulp
Q(EP)(EP)(EP)
Q(OP)(ZQ)(PO)
Q(EOP)Q(PO)
Q(OP)ZQ(PO)
Q-OP-(Q + Paa)-PO
O/O(Q)OP(Paa/Q)PO
Hardwood kraft pulp
QPZP
Q(OP)(ZQ)(PO)
Q(EOP)Q(PO)
Q(OP)ZQ(PO)
O/OZPZP
OPZPZP

Based on European Commission (2013)

Q Acid stage where the chelating agent EDTA or DTPA has been used for the removal of metals, *EP* Extraction stage using sodium hydroxide with the subsequent addition of hydrogen peroxide solution as a reinforcing agent, *EOP* Alkaline extraction bleaching stage using sodium hydroxide with the subsequent addition of oxygen and hydrogen peroxide solution as a reinforcing agent, *EO* Extraction stage using sodium hydroxide with subsequent addition of gaseous oxygen as a reinforcing agent, *P* Alkaline stage with hydrogen peroxide as liquid, *Z* Ozone bleaching using gaseous ozone, *PO* Pressurised peroxide bleaching

Table 4.21 Chemical consumption in bleaching of softwood kraft pulp[a] in Q(OP)(ZQ)(PO) sequence

Brightness, % ISO	89.0
DTPA	2.5
H_2SO_4	20.0
NaOH	34.0
H_2O_2	20.0
$MgSO_4$	2.0
O_2	10.0
O_3	5.0

Based on data from Pikka et al. (2000)

[a] Kappa No. 11

Table 4.22 A comparison of some oxygen chemical bleaching sequences applied to a softwood kraft pulp[a] when the ozone charge is 5 kg/adt

	Brightness, % ISO		
Peroxide charge (kg/odt)	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 4.23 Effect of kappa number after ozone delignification when bleaching softwood kraft pulp[a] in a Q(ZQ)(PO) sequence

	Brightness after (PO), % ISO		
Kappa No. 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

kappa number 12. The ozone charge is 5 kg/ADT. The effect of kappa number after ozone delignification when bleaching softwood kraft pulp of kappa number 12 in a Q(ZQ)(PO) sequence is shown in Table 4.23.

TCF bleaching was first used for sulphite pulps, which are much easier to bleach than kraft pulps. When in the early 1990s the Scandinavian kraft mills started employing TCF bleaching, the main driver was the possibility to take advantage of the developing market for chlorine-free bleached pulp and paper primarily in Germany but also Sweden, the Netherlands, Switzerland and Austria. Initially TCF pulps were also paid a premium compared to conventionally bleached kraft pulp. An additional driver was the expectation that it would be feasible to recycle bleach plant effluents to the chemical recovery system for incineration thereby reducing the effluent load. TCF pulps are produced in a few BKP mills in Brazil, Europe and United States. The following Table 4.24 lists the BKP mills that are employing TCF bleaching. The "fully integrated" mills in Brazil and Sweden bleach only part of the production. Furthermore they may not bleach to full brightness since the entire amount of bleached pulp is directly used in the linerboard/board product. A few BKP mills have the capability to produce both ECF pulps and TCF pulps (Table 4.25).

TCF sequences today 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 fibre strength (Ek et al. 1994; Moldenius 1995, 1997). The lower strength has implications for paper machine

Table 4.24 BKP mills using TCF bleaching

Mill	Wood type	Sequence or bleaching agents used
Smurfit Piteå, Sweden	HW	Fully integrated
Södra Cell Värö, Sweden	SW	O, P, Q
Södra Cell Mönsterås, Sweden	HW, SW	O, Z, P, Q
Korsnäs Frövi, Sweden	HW	Fully integrated
SCA Munksund, Sweden	HW	Fully integrated
SCA Östrand, Sweden	SW	OOQ(OP)(ZQ)(PO)
ENCE Pontevedra, Spain	HW	OOQPQP
Klabin Bacell Camacari,	Brazil HW	OOAhotZP/Fully integrated
Klabin Telêmaco Borba, Brazil	HW	OOQ(PO)(EO)P/Fully integrated
Metsä-Botnia Rauma, Finland	SW	O(ZQ)(PO)(ZQ)(PO/PO)
Evergreen Pulp Samoa, CA, USA	SW	OQQPQ(PO)

Based on Beca AMC (2006)

Table 4.25 Mills using both ECF and TCF bleaching

Mill	Wood/bleaching sequence
Kymmene Pietarsaari, Finland, Line 1	HW OA(Z/D)(OP/P)Z/DP
	OA(Z/Q)(OP)(Z/Q)P
Votorantim Celulose e Papel Jacareí, Brazil, Line B[a]	HW (O/O)AhotZD(PO)1/
	O(OP)Z(PO)
Smurfit Munksjö Aspa Bruk, Sweden	SW OQ(PO) OQ(PO)DD
Mercer Rosenthal, Germany	SW OQOPQZ(PO)P
Mercer Stendal, Germany	SW O(OP)DD(PO)

Based on Beca AMC (2006)

[a] VCP also uses Votorantim Chlorine Free (VCF) bleaching. This is a low-OX ECF with small charge of ClO_2 under controlled conditions (ECF pulp OX = 80–120 g/ADt – VCF pulp OX = 30 g/ADt)

productivity and virgin fibre 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 8 kappa number pulp increases overall wood consumption up to 10 % when compared to an ECF bleaching of 30 kappa number 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 ton of TCF pulp than ECF pulp. This was confirmed at the Enocell (Finland) mill. All the mills that produced any TCF pulp noted its lower strength properties. 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 (Lancaster et al. 1992):

- Capital cost to convert ranges from US$40–$190 million;

- Operating costs increase US$20–$75 per tonne
- Existing bleach plants have insufficient retention time for efficient hydrogen peroxide bleaching.

These estimates in operating cost increases have been by mills that produce both ECF and TCF. An Austrian mill, which modernized its bleach plant to produce ECF, determined that the incremental bleaching cost for TCF would be US$60/t (Haller 1996). The superiority of TCF over ECF bleaching in terms of environmental impact is questionable.

There are some significant disadvantages in TCF bleaching, which explains the lack of interest still being expressed by most of the pulp producers (Chirat and Lachenal 1997). The most important of these is that bleaching a kraft pulp to high brightnesses (90 % ISO) is not possible without sacrificing some strength properties. The problem of cellulose degradation during TCF bleaching has been extensively studied. Taking an OPZ(EO)P sequence for example, it was shown that each stage might contribute to some cellulose depolymerization. One critical factor is the amount of ozone introduced in the sequence. For charges higher than 5–6 kg/t, the cellulose may be slightly depolymerized and oxidized. This last effect makes the pulp sensitive to any alkaline environment such as (EO)P, which leads to further chain cleavage by a mechanism that has already been well documented. Consequently, despite the fact that such a sequence was close to optimum efficiency in terms of delignification (ozone is ranked in the same category as chlorine) and bleaching power, it is penalized by the occurrence of several degradation mechanisms taking place on cellulose in a synergistic way. One possible solution to the problem of cellulose degradation during TCF bleaching to 90 % ISO, is to limit the charge of ozone and to introduce some non degrading bleaching agents in the sequence. The only reagents that demonstrate this property so far are the peroxyacids (peroxyacetic, peroxymonosulphuric acids). But more research is needed to reduce the chemical cost to acceptable levels when peroxyacids are used.

TCF pulps differ qualitatively from ECF pulps (Panchpakeshan 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 sulphite pulps. The viscosity and degree of polymerization (DP) of TCF kraft pulps is based on the type of bleaching sequence and the operating conditions. For achieving the same brightness, TCFz pulp (OZED sequence) had a lower viscosity compared with conventional bleaching (CEDED sequence). 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 (DP) and less number of end groups. Lower hemicellulose retention in TCF pulps also decreases the number of end groups. Reduction in the number of end groups decreases the number of active sites available for intermolecular hydrogen bonding and can result in an overall reduction in the relative bonded area. But this has to be confirmed by further experimental work. Malinen et al. (1994) have reported that softwood TCF pulps tend to show more significant loss in strength properties compared with the hardwood TCF pulps. High consistency ozone-bleached pulps tend to have lower strength properties compared with medium-consistency pulps due to the loss in selectivity of attack by ozone and possible degradation of cellulose at higher concentrations in high-consistency bleaching. The increase in yield from extended delignification is attributed to higher retention of alpha cellulose in RDH pulps. When extended delignification is followed by a TCF bleaching sequence, the yield advantage from higher retention of cellulose is maintained through the bleaching process. Starting from the same kappa number levels, the bleaching yield in TCFz is generally lower by 0.5–1 % compared with ECF bleaching processes (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 are generally less for hardwoods than for softwoods. Lower loss in strength properties for hardwoods may be due to fewer hydrophilic groups in hardwood pulps compared with softwood pulps, lower swelling ability and higher possibility of strength development by refining without losing freeness (Panchapakeshan and Hickman 1997). This must be confirmed by further experimental work. The behaviour of TCF pulps towards heat- and light-induced degradation is different than that of ECF pulps. The higher proportion of carbonyl and carboxyl groups (photoreceptors) account for the accelerated brightness reversion characteristics of TCF pulps. Higher losses in hemicelluloses during extended delignification and TCF bleaching processes are expected to result in a pulp with lower hydrophilicity. Also, with the increased proportion of cellulosic fraction, the pulp is expected to be harder to beat. The beatability of TCF pulps is dictated by the type of bleaching sequence used and the bleached pulp viscosity.

TCFz pulps tend to be more hydrophilic and easier to beat than TCFp pulps. The higher proportion of acidic functional groups is responsible for the higher affinity to water (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 differs 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, 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. First-pass retention is generally expected to increase for TCFZ pulps due to less refining, better fibre swelling ability and, hence, lowest production of fines. Due to the increased hydrophilicity of the pulp, problems may be encountered in the saveall, especially if the saveall is hydraulically limited (Panchapakeshan and Hickman 1997). Optimizing furnish refining and adjusting drainage elements in the forming section will help improve first-pass retention and also lower the amount of fines circulating in the white-water system. Decreasing the fines content helps improve the filtration rate in the saveall and also reduces the sweetener requirement. Increased swelling capacity of fibre results in an increase in the amount of bound water. This can limit water removal in the press section. Modifications required in the press section may include increased press loadings, upgrading the vacuum systems and major changes in press section configuration. Higher press loads may also be necessary to control sheet bulk. Lower strength properties may mean increased sheet breaks in situations where significant open draw exists between the dryer sections. This may require modifications to support the control sheet caliper. However, no significant changes should normally be required in the calendar section.

The measure can be adopted in new and existing kraft mills. In existing mills, using chelating stage, a new oxygen stage and washer is 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 reactor. 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 for peroxide bleaching at new mills with 1500 ADt/d production rate are 7–8 MEuros, with existing pulp mills the costs are 2–5 MEuros depending on the materials of the existing bleaching equipment. If the materials tolerate hydrogen peroxide the costs are 2–3 MEuros. Operating costs with peroxide bleaching are considerably higher, 18–21 MEuro/a, than with ECF bleaching due to the higher chemical costs. If both ozone and peroxide bleaching are applied, the investment costs are higher (European Commission 2001).

4.11 Fortification of Extraction Stages with Oxygen and Hydrogen Peroxide

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. Table 4.26 shows the advantages with oxygen reinforced alkaline extraction. When peroxide is added, it is designated EOP. Figure 4.12 shows the oxygen reinforced extraction stage with hydrogen peroxide (EOP stage). The extraction process reinforced with atmospheric peroxide has gained notability due to its good effectiveness and low capital requirement for implementation. Hydrogen peroxide in alkaline extractions allows a reduction in the use of chlorinated compounds as well as giving a number of quality improvements to the pulp and the bleach plant effluents (Walsh et al. 1991; Anderson 1992; Anderson and Amini 1996). Significant reduction in effluent colour is the greatest benefits of hydrogen peroxide addition in the extraction stage. Other advantages of alkaline extraction with peroxide include improvement of environmental parameters such as COD, BOD and AOX. It is common to use the alkaline extraction reinforced with oxygen (EO) or hydrogen peroxide (EP) or both (EOP, PO), to compensate for lower chlorine dioxide availability and also to make possible the bleaching in short

Table 4.26 Advantages with oxygen-reinforced alkaline extraction

Large savings of chlorine dioxide with a low charge of oxygen
Freedom of process conditions: 65–90 °C (149–194 °F) in atmospheric systems
Option: pressurizing and/or addition of peroxide for further reinforcement
Applicable in all types of sequences, classic chlorine bleaching, ECF and TCF

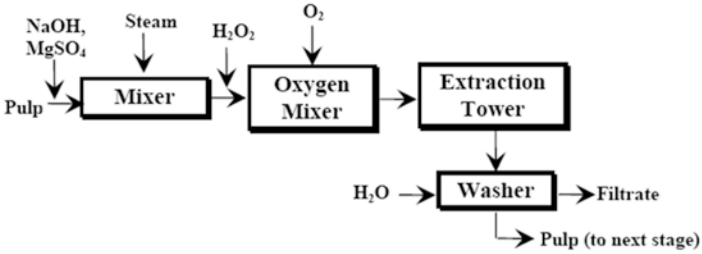


Fig. 4.12 Oxygen-reinforced alkaline extraction (EOP) stage

sequences. When hydrogen peroxide is applied to reinforce the oxidative extraction stage of an ECF sequence, the brightness reversion can also be slightly improved (Young et al. 1992). Hydrogen peroxide can also be used in the second alkaline extraction stage to counteract pulp darkening to reduce chlorine dioxide consumption. Mills also use peroxide to reduce the total applied chlorine dioxide in the final chlorine dioxidestage. The oxidative extraction stages are currently being designed to operate at temperatures of 90 °C or higher and at pressures more than 75 psig in order to obtain the maximum effect from oxygen and added peroxide (Bajpai 2012b).

However, peroxide reinforcement can be more effective when pressurized in the so-called PHT -stage technology (Pereira et al. 1995; Breed et al. 1995). The most common types of alkaline extractions now a days are those reinforced with oxygen and peroxide, partially pressurized (EOP) or pressurized all the way, the so-called (PO)-stage. For a softwood kraft pulp (kappa factor 0.18), the use of oxygen and hydrogen peroxide in the extraction stage (EOP) results in reduction on kappa number after extraction from 3.5 to 2.5. Bleach plants that have a low availability of chlorine dioxide and require high peroxide dosages (0.8–1.0 %) needs more severe conditions for peroxide consumption. In these cases, pressurized peroxide stages such as (PO) or PHT are recommended, because they allow 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; Süss 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).

A more powerful oxygen extraction stage is accomplished by raising the temperature in the stage, increasing the oxygen charge, pressurizing the pre-retention tube and adding hydrogen peroxide. The most important factor is temperature. Use of pressurized peroxide stages (PO) makes possible to achieve a high final brightness in totally chlorine free (TCF) bleaching (Anderson and Amini 1996; Bajpai 2012b; 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, e.g. manganese, copper and iron, is low. Several mills around the world are using oxygen-peroxide reinforced extraction stage.

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

Table 4.27 Conditions in an EOP stage[a]

Pulp consistency	%	10–15
Temperature	°C	60–70
Charge of NaOH	kg/Adt	0.8–1.2 x Kappa No.
Charge of O_2	kg/Adt	3–5 (7)
Charge of H_2O_2	kg/Adt	0–3
Pressure	bar	1.5 (3–4)
Oxygen treatment	min	5–15 (30–60)
Total retention time	min	30–90
pH (final)		10–11

[a] Conditions given in parenthesis refer to a more powerful extraction stage

stage can improve the brightness and delignification for a particular level of hydrogen peroxide (Troughton and Sarot 1992). Process conditions in extraction stage in most pulp mills are generally sufficient to efficiently utilize the added hydrogen peroxide. Table 4.27 shows conditions in a EOP stage.

4.12 Removal of Hexenuronic Acids

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 paper making process; they reduce bleaching efficiency by consuming a disproportionate amount of bleaching chemicals. When the bleaching chemicals are being consumed in non-essential reactions, there is a decrease in the efficiency of the chemicals, as well as the cost efficiency of an operation (Chai et al. 2001; Vuorinen et al. 1996; Bergnor and Dahlman 1998). Some studies have shown that the consumption of bleaching chemicals correlates with the amount of HexA groups in hardwood kraft pulps. Approximately 35–55 % of elemental chlorine-free (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 non-process elements, which can cause loss of efficiency and accelerate deposit buildup on process equipment (Laine et al. 1996). It also binds

Table 4.28 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
Increased brightness reversion
May increase binding of transition metal ions, thus may increase the use of chelating agents in hydrogen peroxide bleaching
May contribute to the formation and deposition of oxalates on bleaching equipment

Based on Bajpai (2012b) and Vuorinen et al. (1999)

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 correlates with kappa reduction, as these groups consume part of the potassium permanganate used in this determination (Li and Gellerstedt 1997a, b; Chai et al. 2001). Since kappa number is widely used for the evaluation of delignification efficiency in cooking and bleaching process, the presence of HexA affects the results of this analysis and thus give 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 4.28 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. Following methods have been examined for selective removal of HexA:

- Hot acid stage (Ahot) (Henricson 1997; Van Jiang et al. 2000)
- Combined hot acid and hot D stage (AD)hot (Ragnar 2002)
- High temperature D stage also called hot D stage (designated DHT or Dhot) (Lachenal et al. 2000; Eiras and Colodette 2003; Lindstrom 2003)

4.12.1 Hot Acid Stage (Ahot) or Combined Hot Acid and Chlorine Dioxide Stage (AD)hot

HexA can be removed through mild acid hydrolysis which results in bleaching chemical savings. The extent of savings and economical viability of adopting this process (new tower and washer stage) is dependent of the HexA content of the pulp and effective chemicals reduction verified without yield loss and degradation of pulp quality (Pikka et al. 2000; Furtado et al. 2001; Marechal 1993; Lachenal and Papadopoulos 1988; Vuorinen et al. 1996; Hosoya et al. 1993; Fatehi et al. 2009). The conditions for mild hydrolysis are: pH 3–3.5, temperature 85–95 °C

Table 4.29 Typical conditions for (A) hot and (AD) hot stages

Parameter (Unit)	(A) hot	(AD) hot
pH	3–4	3–3.5 (A), 2.5–3 (D)
Temperature (°C)	90–110	90–95 (A), 80–85 (D)
Time (minutes)	60–180	120 (A), 15–30 (D)

Based on Beca AMC (2006)

and time 120–180 min. The first whole bleaching sequence where an A-stage was combined with bleaching was applied at Aracruz Pulp Mill in 2002 (Brazil). Later, it was applied in other South American mills using high HexA content eucalyptus pulps. The A –stage is applied without interstage washing before the chlorine dioxide stage (D0) or the initial ozone stage (Z) but in this last configuration also with an interstage washing. Table 4.29 lists the typical conditions for these types of hot acid stages.

A hot acid stage (Ahot) usually precedes a first dioxide stage (D0) or a ZMC stage. The objectives are to reduce the charge of chlorine dioxide or ozone and to decrease brightness reversion of the fully bleached pulps. A hot acid stage (Ahot) is a fully equipped stage within a bleaching sequence. In other words the pulp is washed after the acid treatment before heading for the next stage. In (AD)hot two stages have been combined in one stage. The procedure is: acid treatment, no intermediate washing, chlorine dioxide bleaching, washing. Hence, one washing unit has been omitted. The reported savings in chlorine dioxide vary considerably (1–2 and up to 3 kg/ADt as chlorine dioxide), when complementing a conventional D0 stage with an Ahot stage or replacing a conventional D0 stage with an (AD)hot stage in ECF bleaching of eucalyptus kraft pulp. These are actual mill data. In general, AOX decreases with a decreasing charge of chlorine dioxide. When (AD)hot is introduced, the observed decrease in AOX formation is due to lower chlorine dioxide consumption, but may also be due to lower AOX formation as such. A consequence of the severe process conditions (time, temperature and pH) in Ahot and (AD)hot stages is a strong acid hydrolysis, which effectively removes not only HexA but also hemicelluloses and degrades the cellulose. It is, therefore, likely that the total yield will decrease (wood consumption will increase) and also that the formation of COD will increase. With regard to pulp quality, the major benefit of replacing a conventional D0 stage with Ahot and (AD)hot stages is a decrease in brightness reversion. Pulp strength and pulp refinability may decrease or remain the same. Some mills have been retrofitted with hot acid stages, Ahot or (AD)hot. A few examples are: the Aracruz, Guaiba, Brazil BEKP mill in 1999 – ECF sequence (AD) EDEDW (Ratnieks et al. 2001) and Votorantim Celulose e Papel (VCP), Jacareí, Brazil BEKP mill, Line B in 2000 – ECF sequence (O/O)AZD(PO) (Rodrigues da Silva et al. 2002). Table 4.30 lists the benefits reported by these mills which could be attributed exclusively to the installation of the hot acid stage.

Table 4.30 Benefits of using hot acid stage in bleached eucalyptus kraft mills

Reduced consumption of chlorine dioxide (active chlorine)
Reduced oxalate scaling
Reduced brightness reversion
Increased level of metal ions in the digester washing zone with closure of the A stage
Good performance of the recovery boiler despite the increased level of chloride with closure of the last bleaching stage

Based on Beca AMC (2006)

A hot acid stage is also operating at the Klabin Bacell, Camacari, Brazil, BEKP mill – TCF sequence OOAZP and has been trialled at the VCP, Luiz Antonio, Brazil BEKP mill – ECF sequences (O/O)A(ZD)(EOP)D and (O/O)AD(EOP)(ZD) and CENIBRA, Bel Oriente, Brazil BEKP mill – ECF sequence OADEDED (Gomes da Silva et al. 2002; Costa and Colodette 2002; Beca AMC 2004). During 2002/2003 a new kraft eucalyptus fibreline was started up at Aracruz, Barra do Riacho, Brazil with a bleach plant including a hot acid stage, (AD)hot(EOP)(DD). Experience so far supports around 15–20 % savings in chlorine dioxide consumption, somewhat reduced AOX formation, higher COD formation and less brightness reversion, when compared to an initial D0 stage. Hot acid stages do not brighten the pulp although efficient in removing HexA, and thus reducing the consumption of chlorine dioxide and decreasing the brightness reversion. In addition such stages may decrease pulp yield, strength and refinability and also require significant capital for installation. The savings in chlorine dioxide vary considerably and depend on eucalyptus species, number of bleaching stages, bleachability of the pulp and process conditions in pulping. Thus, despite a few application in the Brazilian BEKP mills, adoption of acid hydrolysis as a standalone stage, Ahot or (AD)hot, has not been widespread (Eiras and Colodette 2003) and is debatable as an environmental measure.

4.12.2 High Temperature Chlorine Dioxide Stage (DHT)

This technique is similar to (AD)hot (acid hydrolysis followed by chlorine dioxide without interstage washing) technology, except that the addition of chlorine dioxide occurs at the beginning of the stage. The DHT stage is based on the principle that the reaction rate of chlorine dioxide with lignin is faster than that with HexA. Hence, the majority of the chlorine dioxide is consumed by lignin at the beginning of the reaction, while the HexA are eliminated later through acid hydrolysis at high temperature and long exposure (Eiras and Colodette 2003). The main motivations for applying the DHT stage in ECF bleaching of eucalyptus kraft pulps are potential reductions in capital costs (shorter sequences), operating costs and increased pulp brightness stability ((Eiras and Colodette 2003). The DHT stage is more efficient than a conventional first D stage (D0). It decreases bleaching chemical costs and the formation of AOX in ECF bleaching. This is particularly true for three-stage sequence bleaching, which requires an extracted kappa number of ~3.5. However, the DHT stage usually negatively affect the pulp yield, viscosity/strength, and refinability, which can offset the economic gains. Moreover, the filtrate, rich in metal ions and organic matter (increased COD formation), may be difficult to manage. For long sequences, 4–5 stages, the gains due to a DHT stage can be negligible and, probably, do not justify its implementation. However, it must be considered, that this technology can be a unique alternative in bleaching eucalyptus pulp to 90 % ISO brightness, with acceptable chemical consumption, in a three-stage bleaching sequence (Eiras and Colodette 2003). Shorter sequences are being used to reduce the capital costs (Ragnar and Dahllöf 2002; Süss and Del Grosso 2002; Eiras and Colodette 2003; Leporini Filho et al. 2003). There are some kraft eucalyptus mills operating or coming into operation with bleach plants including a DHT stage, e. g. CENIBRA, Bel Oriente, Brazil, DHT(EO)DED (2002); Ripasa, Limeira, Brazil, DHT(OP)D (2003); CMPC, Santa Fé, Chile, DHT(EOP)D (2003/2004); Suzano, Mucuri (Bahia Sul) DHT(EOP)D(PO) (2004) and Mondi, Richards Bay, South Africa, DHT(OP)DD (2005).

Despite the positive effects of Ahot, (AD)hot and DHT, possible drawbacks are : increased yield loss (increased wood consumption), decreased pulp viscosity/strength and refinability and increased COD in bleach plant effluents The positive and negative effects of the three modes of ‘hot acid’ or hot D stages vary considerably depending on the eucalyptus species, the number of bleaching stages, the bleachability of the pulp and the process conditions in pulping and bleaching. Usually both the advantages and drawbacks are more accentuated for Ahot and (AD)hot than for DHT. There are a number of ‘hot acid’ or hot D in operation or coming into operation in BEKP mills. The rationale for, and effects from, the implementation of any of the stages must be evaluated from case to case.

4.13 Liquor Loss Management

Black liquor may be lost from the kraft mill at several locations in the fibreline and recovery areas. Due to the organic matter present in black liquor, losses of black liquor are of much greater concern than losses of green or white liquors. The organic fraction of black liquor is composed of degraded lignin; wood sugars; carboxylic and hydroxy acids; extractives consisting of resin acids, fatty acids, and neutral compounds such as sterols and a variety of other compounds. The composition of a black liquor depends on the wood species from which it was generated. The various types of compounds are removed to different degrees in biological treatment systems. Wood sugars, formic and acetic acids are readily biodegradable, exerting a BOD load on treatment systems. Lignin degradation compounds are not readily biodegraded; they pass through treatment into the effluent, contributing COD and colour. The extractives are somewhat biodegradable but may produce toxic effects in treatment systems and final effluents (Stratton and Gleadow 2003). In almost all kraft mills, leakage from seals on pumps, agitators, and other rotating equipment occurs. Certain events may generate wastewaters containing black liquor, including startups, shutdowns, and cleanings of storage and process vessels. Most black liquor evaporators do not have continuous losses, although carryover of liquor into evaporator condensates may occur, particularly in older rising-film design units, units with poor mist eliminators, or units that are heavily loaded. Evaporator boilouts may result in losses of dilute black liquor. Boilouts are initiated every few days or weeks to remove water-soluble scales that reduce heat transfer performance. A boilout involves shutting off the liquor feed and purging the system with clean water or thin liquor while maintaining steam flow. As the product liquor becomes more dilute, the boilout liquor is diverted to a tank for later recovery. Few mills recover all of the boilout stream, while others divert the most dilute portions to the wastewater system. Factors which may affect specific practices at mills include value of the recovered chemicals and energy, treatment cost and capacity, evaporation cost and capacity, effluent discharge limitations, or other constraints. A review of mill spill management practices shows that, in the absence of such constraints and using assumptions to represent a typical ECF bleached kraft mill, recovery of dilute black liquor directly to the evaporators becomes uneconomic at concentrations below about 4 % black liquor solids (Amendola et al. 1996). However, recovery of black liquor is often practiced down to a concentration of 0.5 % solids (McCubbin 2001a). The recovery of tall oil and turpentine byproducts are activities with potential to generate potent wastewaters that can affect treatment performance and effluent quality. In most of the mills these byproduct recovery areas are isolated from the mill wastewater collection system so that any spills can be recovered. These materials contain high levels of BOD and COD and are found to be toxic to treatment plant biota and effluent bioassay test organisms. EPA in its Cluster Rule regulation promulgated in 1998 included best management practices (BMPs) for spent pulping liquors, tall oil soaps, and turpentine (USEPA 1998a). Bleached chemical, soda, and stand-alone semi-chemical pulp mills are required to comply with the BMPs. Inclusion of BMPs indicates an increasing focus on the importance of fibreline and recovery area wastewaters from chemical pulp mills.

The chemical recovery area should be designed according to the spill management concepts. Spill and buffer tank capacity needs to be determined as part of an engineered system (USEPA 1998b). Tanks should be large enough so that process changes can be made to avoid unplanned overflows, but not so large as to enable unbalanced operating conditions to continue without corrective action being taken. Their use needs to be integrated into normal operating strategies, since very large buffer and spill tanks often operate at full capacity and their contents may not be recycled back into production as part of normal operation. Spill control can be one of the most cost-effective method by which a mill can reduce effluent loads. It can be especially effective at reducing colour loads, since black liquor losses can represent a significant contribution to colour and conventional effluent treatments do not remove colour efficiently. Managing liquor losses involves both behavioural and equipment aspects. A review of mill spill management practices showed that mills achieving the lowest levels of liquor loss emphasised preventive measures to avoid the need for spill recovery (Amendola et al. 1996). Conventional bleached kraft mills with untreated effluent COD of roughly 40 kg/ADt would be considered to have good spill control. Mills with oxygen delignification would be expected to be at about 30 kg COD/ADt. However, many other factors could influence these values (McCubbin 2001a). To increase preventive measures, mills typically have spill recovery sump pumps in critical areas that are automatically activated when a stream monitoring parameter, usually conductivity, exceeds a set point value. Design of sumps should be appropriate for the size and type of spills likely to be encountered. The objective is to recover the spilled material and return it to the black liquor system with minimal contamination. Water is a contaminant, as it must be subsequently removed from the recovered spill. Some mills isolate clean water streams (example seal water) by running them into separate pipes laid on the bottom of floor drains (McCubbin 2001b).

4.14 Condensate Stripping and Recovery

In-plant treatment of waste condensate has become an accepted method for the removal of odorous gases and BOD (Stratton and Gleadow 2003). This treatment is required for environmental reasons as the pollution control regulations have become increasingly stringent (Burgess 1993). Weak black liquor from brownstock washing contains about 15 % dissolved solids (85 % water) by weight. Before firing the liquor in a recovery furnace, it is concentrated to 60–85 % dry solids. Therefore, for each kilogram of black liquor solids (BLS), about five kilograms of water must be removed. The majority of this water removal is performed in multiple effect evaporator sets, each consisting of a series of vessels equipped with heat exchangers. Fresh steam enters the first effect, which operates above atmospheric pressure to evaporate water from the most concentrated liquor. The resulting water vapor (low pressure steam) passes to the next effect, which operates under a lower pressure, to evaporate additional water, and so on. The final effects of the evaporator train are under vacuum. Condensates are generated in each effect as the vapors transfer heat to the liquor (Stratton and Gleadow 2003). The initial vapors from boiling the weak black liquor, typically condensed in the final effects and surface condenser, contain most of the volatile components of the liquor. The volumes of evaporator condensates generated are substantial. A mill with an evaporator load of 5 kg water/kg BLS and 1500 kg BLS/ADMTP would produce at least 7.5 m^3/ADMTP of evaporator condensates. Actual volumes generated may be substantially higher in evaporator sets equipped with barometric condensers, which can add from 2 to 45 m^3 cooling water per ADMTP (Blackwell et al. 1979). Table 4.31 shows typical pollutant loads in foul condensates (bleached kraft mill) and Table 4.32 shows the heat value of pollutants.

Modern evaporator systems use non-contact surface condensers to condense the final vapors. Additional condensate volumes are generated by using vacuum pumps or steam ejectors used to provide vacuum. Evaporator condensates contain

Table 4.31 Typical pollutant loads in foul condensates in bleached kraft mill[a] (softwood)

Source	Total flow kg/tonne	Methanol kg/t b/t	Turpentine kg/t	Total reduced sulphur kg/tt
Batch digester mill				
Digester accumulator overflow	1125	4.0	0.50	0.20
Turpentine decanter underflow	250	1.5	0.50	0.15
Total evaporator condensate	7000	4.2	0.25	1.00
Continuous Digester Mill				
Turpentine decanter underflow	450	2.5	0.50	0.12
Total evaporator condensate	8000	7.5	0.50	1.20

Based on Lin (2008)

[a] Based on unbleached digester production

Table 4.32 Heat value of pollutants

Pollutant	Net heat of combustion (kgcal/kg)
Methyl akcohal	5037
Alpha-pinene	9547
Hydrogen sulphide	3647
Methyl sulphide	6229
Dimethyl sulphide	7371
Dimethyl disulphide	5638

Based on Lin (2008)

the volatile low molecular weight compounds present in black liquor, including alcohols, ketones, terpenes, phenolics, organic acids, reduced sulphur compounds, and others. Methanol is the primary constituent, accounting for up to 95 % of the total organic content of condensates. Methanol is easily biodegraded. Each kilogram exert about 1 kg BOD5. The total BOD5 load from condensates has been reported to be about 8 to 12 kg/ADMT pulp (Blackwell et al. 1979). Evaporator condensates are typically segregated according to their level of contamination, with the goal of reusing the cleaner fractions and reducing the volume requiring treatment. There are many different segregation schemes in use at mills. A simple scheme involves collection of the most contaminated condensates from the sixth effect and final surface condenser in one stream, and all the remaining condensates in a second, larger, combined stream. The evaporator foul condensate stream would then typically be combined with other foul condensate streams from the digester area before treatment in a steam stripper or biological treatment plant to reduce the release of hazardous air pollutants (HAPs). The combined condensates and stripped foul condensates are often used as wash water on the final brownstock or post-oxygen washer, and sometimes for mud washing in the causticizing plant. In most mills, the available volume of condensates exceeds the total requirement of these two areas, and the excess becomes wastewater. There are other process areas such as the bleach plant where there is a need for clean hot water. Because condensates are hot and have very low concentrations of metals, they are potentially attractive hot water sources, particularly in peroxide-based bleach plants where transition metal ions have harmful impact. Condensates also have very low hardness (calcium and magnesium) levels and may reduce scaling in mills with hard process water. Due to their COD and reduced sulphur compound content, additional treatment may be required before reuse in the bleach plant would be considered in many mills. However, it has been shown that even highly contaminated condensates (COD of 6218 mg/L) had only minor effects on peroxide or ozone bleaching performance or pulp quality, and the bleached pulps were free from unpleasant odors (Annola et al. 1995).

In Sweden, Sodra Cell's Varo mill reported on its operation of a second condensate stripper to clean evaporator condensates having a COD of 2000 mg/L. The unit was installed with and is integrated into a new evaporator set. Performance was reported to be 90 % removal of COD and greater than 95 % removal of reduced sulphur compounds. The unit has enabled the mill to reuse all its condensates and eliminate fresh water use in the bleach plant during normal operation. Bleaching is done with a peroxide-based TCF sequence. Benefits from lower peroxide use for bleaching and better pulp strength, presumably due to lower metals concentrations, were also reported (Emilsson et al. 1997). Improvement in effluent toxicity response resulting from the use of a reverse osmosis (RO) treatment for "clean" (COD of 1067 mg/L) condensate from the fifth effect of the evaporators at the Irving Pulp & Paper mill in St. John, New Brunswick, Canada has been reported (Dubé et al. 2000). The RO unit uses a three layer composite membrane and concentrates at least 88 % of the BOD and COD in a volume representing 1 % of the feed volume. The concentrate is burned in the bark boiler or with the black liquor in the recovery furnace. The treated condensate is used for brownstock washing. Mill effluent, which is not biologically treated, produced a much lower toxicity test response when the RO unit was operating.

Other methods have been suggested for cleaning condensates before reuse. These are aerobic biological treatment using a high temperature membrane bioreactor (Bérubé and Hall 2000). The advantages of reusing the condensate streams are:

- Reduction in energy
- Reduction in water use
- Reduction in effluent flow

The chemical constituents in evaporator condensates are usually removed to a high degree in mill effluent treatment plants anyway, so unless the treatment plant is heavily loaded, few benefits are expected in treated effluent quality due to separate treatment of condensates. Combustion of methanol, in a boiler or incinerator converts all of the carbon to carbon dioxide and water. Methanol has a fuel value of 21 MJ/kg, and this has the potential to offset a substantial portion of the energy required for steam to strip the condensates. Biological treatment, in a mill's effluent treatment plant or a dedicated unit, will convert a portion of the organic carbon into biological solids, which requires dewatering and disposal.

These strong condensates are generally treated in a stripper where the removal efficiency for most compounds is more than 90 % depending on the pH. Stripping systems usually remove malodorous gases and COD-contributing substances at the same time. Stripped condensates after treatment can be 1–1.5 kg COD/m^3 of condensate. The stripped gases can be inserted to CNCG system and handled appropriately. These gases can be incinerated in a dedicated burner, the recovery boiler or the lime kiln. About 7–9 m^3 of weaker condensates with medium and low contamination are produced with COD ranging from 0.5 to 2 kg COD/m^3 containing a total of about 8–12 kg of COD/t of pulp. Moderately-contaminated condensates can also be stripped in a system linked to the evaporation plant thus effecting treatment without any substantial additional use of energy. In this way the total COD load before any reuse is reduced by about 50 % compared to only treating the most contaminated condensates. The stripping column can be a separate piece of equipment or it can be an integrated part of the evaporation plant. The condensates are fed to the top of the stripping column. Steam or vaporised condensate rises from the bottom of the column in a countercurrent manner to the foul condensate. The overhead vapour from the stripping column is sent to a reflux condenser where it is partly condensed. The purpose of the reflux condenser is to condense some of the water and to increase the concentration of volatile material in the gases leaving the condenser. The non-condensable gases (NCGs) from the condenser contain the majority of the volatile compounds that are stripped in the stripping column. They are led to incineration where the organic and TRS compounds are destroyed by thermal oxidation. Cleaned condensates are free of metals and therefore are particularly useful for washing in the bleach plant when aiming at closing up this part of the process. They can also be reused in brown stock washing, in the causticising area (mud washing and dilution, mud filter showers), as TRS scrubbing liquor for lime kilns or as white liquor make-up water. This means that some condensates will be used in closed parts of the process and will not be discharged to waste. Other condensates will be used in open parts, example the bleach plant, and end up in the effluent together with those condensates, which are not reused but discharged directly to waste.

When steam stripping is used, the NCGs have to be incinerated separately in order to avoid release of concentrated TRS gases into the atmosphere. When the stripping of concentrated, contaminated condensates is used, the load to the waste water plant will be reduced and if there are difficulties to meet the permit, new investments in the effluent treatment plant may be avoided. This also means that less energy is required for aeration and less energy and chemicals in the sludge treatment. When combining the recovery of clean condensates and stripped condensates, fresh water consumption may be decreased by 6 m^3/ADt. Because the condensates are hot, part of the energy used in the stripping column can be saved. Fugitive TRS emissions from waste water treatment plants can be reduced by the steam stripping of condensates which removes TRS compounds from foul condensates. As the stripper off-gases contain 8–12 kg/ADt methanol, there is the potential to save fuel oil or natural gas, provided that the stripper gas can replace the fuel.

The stripping of contaminated condensate is common in most mills. When the stripping system is used for high methanol removals, the condensates from the stripping column are relatively clean and can be reused in the pulp mill for applications such as brown stock washing. The basis for the design should be the minimisation of the flow to the stripping system by segregating the condensates in order to reduce the required investment. In the evaporation plant, the first liquor vapour condensate can be split into two fractions. Surface condenser can be split into two units or two condensing steps. The blow vapour from a batch digester can be condensed in two steps. Secondary steam can be used as the main steam source to the stripping column. The best place to reuse the condensates is pulp washing either on the last washer or on the decker in a mill with a closed screen-room water system. The typical wash water demand is 10–13 m^3/ADt. The evaporator-area and digester-area condensate available for reuse can amount to 6–9 m^3/ADt, which is the amount of potential water savings. In total the stripping of only the heavily polluted condensates would result in 4–6 kg COD/ADt while with stripping of the condensates with medium contamination, about 3–5 kg COD/ADt can be obtained. However, condensates discharged to effluent treatment are mostly readily biodegradable. TRS removal is about 97 % from the condensate, methanol removal about 92 % (European Commission 2013).

Steam stripping can be applied at both new and existing kraft mills. The condensate stripping column can be separate or it can be integrated into the evaporation plant. In the former case, live steam would be required whereas in the latter case, secondary steam from evaporator effects can be used. However, thermal oxidation of the vapours from the stripper system is needed. Lime kilns, power boilers and separate TRS incinerators can be used for this purpose.

The investment required for the stripper system at a 1500 ADt/d kraft pulp mill is about EUR 2.0 million – 2.5 million (European Commission 2013). Additional investment may be required to increase the capacity of the evaporation plant of the mill, but this depends very much on the existing evaporation plant configuration. Retrofitting costs can vary between EUR 1 million and 4 million. The operating costs of condensate stripping consist mainly of the cost of steam used in stripping and maintenance. If the stripper is operated separately from the evaporation plant, the operating costs are significantly higher due to the demand of fresh steam. The costs are about EUR 0.6 million – 0.7 million/year. If the stripper is connected between the evaporation stages, the operating costs are lower. The operating costs in the latter case are EUR 0.3 million – 0.4 million/year.

The majority of kraft pulp mills in Europe carry out the steam stripping of contaminated condensates from the cooking and evaporation plant. The stripping of contaminated condensates efficiently removes its odorous components (Urbanski et al. 1998). Stripped condensates may be reused in unbleached and bleached pulp washing and in causticising processes thus achieving a reduced water consumption. Numerous mills in Europe are using this approach (Sebbas 1988).

Catalytic oxidation has been developed for treatment of condensates and odorous gases (Norvall et al. 2001). The use of catalytic oxidation provides a low capital cost option for treatment of condensates and odorous gases. ODORGARD™ is best described as catalytically enhanced wet scrubbing. Wet scrubbing, using sodium hypochlorite, has been used to treat TRS gases generated at sewage treatment works, and meat rendering plants (Stitt and Fakley 1995). The Domtar Papers mill in Cornwall, ON, has long used a hypochlorite scrubber to treat odors from the batch digesters (Bonsu et al. 1986). The ODORGARD® Process, marketed in Australia and New Zealand by Orica Watercare under licence from Johnson Matthey PLC, offers catalytically enhanced odour and low-level VOC destruction, using a heterogeneous supported catalyst in a fixed-bed reactor. With patents for both the catalyst and process applied for or granted around the world, the ODORGARD® Process is recognised as a unique and practical solution to a high profile environmental problem. Based on conventional alkaline bleach scrubbing the ODORGARD® Process utilises a catalyst to convert the sodium hypochlorite molecule into brine and a highly reactive oxygen atom held on the surface of the catalyst. The reaction which takes place over the catalyst can be summarised thus: It is this oxygen species which is responsible for the enhancement in scrubbing efficiency both in the level to which particular compounds are oxidised and the range of compounds that can be oxidised.

4.15 Reduction of Sulphur Oxides and Nitrogen Oxides Emissions

Forest products manufacturing is one of many industrial sources of sulphur oxides (SOx) and nitrogen oxides (NOx) emissions (NCASI 2013). They originate as products of combustion that accompany steam and power generation, processing of pulping chemicals, and wood drying. In the United States, electric utilities are by far the dominant sector for SOx and NOx emissions. In Canada, smelting (for SOx) and upstream oil and gas (for NOx) sectors dominate these releases. Since the 1980s, measures have been taken in North America to reduce atmospheric emissions of SOx and NOx where levels contributed to impaired environmental quality, as well as in response to government mandated performance standards. Considered together, these substances have been implicated in adverse respiratory effects where certain thresholds are exceeded, as well as acidic deposition thought to be of consequence to vegetation, soils, and surface waters. NOx emissions are also known to contribute to ozone formation and deposition-related eutrophication of surface waters. Most recently, SOx and NOx emissions are being scrutinized because of their role in the formation of fine particulate matter, which is an emerging health concern and a contributor to visibility impairment in certain geographic settings (USEPA 2007). SOx and NOx emissions are both largely the result of combustion processes. In the United States, SOx emissions are dominated by stationary sources, foremost among them electric utilities. The fuel combustion-related emissions from utilities are about five times those associated with industrial fuel combustion, the second largest source. NOx emissions are dominated by mobile sources, which are nearly three times as great as those from utility and industrial fuel combustion combined. Emissions reductions since the 1980s have been dramatic. Ambient air quality

Table 4.33 Prominent Pulp and Paper Industry sources of SOx and NOx (10^3 tons)

Source	SOx	NOx
Power boilers	205	124
Kraft recovery furnaces	29	55
Kraft lime kilns	2	8
Kraft thermal oxidizers	1	1

Based on NCASI (2013)

standards for NO_2 are universally met across the United States, and the new more stringent short-term sulphur dioxide standards are exceeded in just four limited areas in the nation (USEPA 2011). Further reductions in ambient concentrations will occur due to revision of performance standards, declining use of coal by electric utilities and industrial sources, and requirements that utilities and industry address emissions that contribute to regional haze and ozone.

The most prominent source of SOx and NOx emissions at a pulp and paper mill is the power boilers that generate steam and electrical energy for the manufacturing process. Both SOx and NOx are the result of the combustion of sulphur- or nitrogen-containing fossil fuels and non-fossil fuels, respectively. Emission levels are driven largely by the choice of fuels, principally fossil fuels fired alone or in combination with wood-derived fuels, along with the facility's approach for controlling these emissions either in situ or post combustion. The magnitude of boiler emissions in 2010 relative to those from process sources is illustrated in Table 4.33. In the pulp and paper industry, SOx is typically measured as SO_2. NOx is made up of NO and NO_2, and all the NO is reported as though it were NO_2 (NCASI 2012).

Kraft recovery furnaces are the second largest source after power boilers. Together, boilers and recovery furnaces constitute approximately 98 and 92 % of the pulp and paper sector's SOx and NOx emissions, respectively. The pulp and paper industry has a history of reducing emission levels of SOx and NOx. Practices that have been applied or have potential application include

- Increased energy efficiency
- Use of alternative fuels with low nitrogen and sulphur content or lower emission potential
- Decreasing the moisture content and increasing the heat value of pulping liquors fired in recovery furnaces
- Optimization of combustion conditions
- Growing use of add-on control technologies

For its part, the pulp and paper industry has had a sustained reduction in emissions of SOx and NOx since the 1980s. In the United States, sulphur dioxide emissions have declined over 70 % from 1980 levels despite increases in production. NOx emissions in 2010 were 30 % lower than in 1980. In Canada, sulphur dioxide emissions decreased by 51 % between 2001 and 2010, from 2.29 kg/tonne to 1.13 kg/tonne (production-weighted mean). NOx emissions in Canada were more consistent during this period of time, but were reduced by 11 %, from 1.42 kg/tonne

Table 4.34 Range of observed emissions of SOx and NOx from recovery furnace and lime kiln

Emission source		SO_X	NO_X
Recovery boiler	Observed emission levels	~0 to 300 ppm	40–130 ppm
	Best available control technology	50–300 ppm	75–150 ppm
Lime Kiln	Observed emission levels	~0 to 20 ppm	30–350 ppm
	Best available control technology	30–80 ppm	30–300 ppm

Based on NCASI (2013)

to 1.27 kg/tonne (production-weighted mean). These reductions, in part, reflect a response to technology-driven regulatory standards, equipment modernization, improved operating and energy efficiency, alternative fuel selection, and industry restructuring. Table 4.34 illustrates the range of observed SOx and NOx emissions from various pulp and paper mill sources, along with emission levels derived on the basis of control technology benchmarks (NESCAUM 2005; European Commission 2001; NCASI. 2013).

Flue gas treatment (FGT) is more effective in reducing NOx emissions than are combustion controls, although at higher cost. FGT is also useful where combustion controls are not applicable. Pollution prevention measures, such as using a high-pressure process in nitric acid plants, is more cost-effective in controlling NOx emissions (World Bank 1998). FGT technologies have been primarily developed and are most widely used in Japan and other OECD countries. The techniques can be classified as selective catalytic reduction, selective noncatalytic reduction, and adsorption. Selective catalytic reduction (SCR) is currently the most developed and widely applied FGT technology.

SCR is the most advanced and effective method for reducing NO_x emissions and can do so by up to 80–90 %. SCR entails the reaction of NO_x with ammonia within a heterogeneous catalytic bed in the presence of oxygen at temperatures normally in the range of 523–673 K. The predominant reactions are (Radojevic 1998):

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$

NH_3 is chemisorbed on a catalyst and reacts with NO_x in the gas phase. Many catalysts with varying operating temperature windows may be used. The performance of SCR is affected by temperature, NH_3/NO_x ratio, oxygen concentration, catalyst loading and the type of catalyst support used (Radojevic 1998). Depending on the process parameters, various catalysts have been studied for NH_3-SCR including noble metals, metal oxides and zeolites. The catalyst is usually a mixture of titanium dioxide, vanadium pentoxide, and tungsten trioxide (Bounicore and Wayne 1992). No catalysts have been reported to be active at temperatures above 873 K or below 523 K. It is also possible to achieve SCR by using hydrocarbons as a reducing agent (HC-SCR). However, at temperatures above 773 K all of the hydrocarbons are consumed by combustion reactions. Overall the application of SCR to CFBC is problematic due to high risks of poisoning by sulphur dioxide and vapours of volatile metals, alternating oxidising and reducing atmospheres, and the low operating temperatures of 150–180 °C after the boiler and de-dusting (Tran et al. 2008). Unfortunately, the process is very expensive (US$40–$80/kW), and the associated ammonia injection results in an ammonia slipstream in the exhaust. In addition, there are some concerns associated with anhydrous ammonia storage. SCR can remove 60–90 % of NOx from flue gases.

Selective noncatalytic reduction (SNCR) using ammonia- or urea-based compounds is still in the developmental stage. Early results indicate that SNCR systems can reduce NOx emissions by 30–70 %. Capital costs for SNCR are expected to be much lower than for SCR processes, ranging between US$10 and US$20 per kilowatt (Bounicore and Wayne 1992). Several dry adsorption techniques are available for simultaneous control of NOx and sulphur oxides (SOx). One type of system uses activated carbon with ammonia injection to simultaneously reduce the NOx to nitrogen and oxidize the sulphur dioxide to sulphuric acid. If there is no sulphur in the fuel, the carbon acts as a catalyst for NOx reduction only. Another adsorption system uses a copper oxide catalyst that adsorbs sulphur dioxide to form copper sulphate. Both copper oxide and copper sulphate are reasonably good catalysts for the selective reduction of NOx with ammonia. This process, which has been installed on a 40-MW oil-fired boiler in Japan, can remove about 70 % of NOx and 90 % of SOx from flue gases (Cooper and Alley 1986).

The most cost-effective methods of reducing emissions of NOx are the use of low-NOx burners and the use of low nitrogen fuels such as natural gas. Natural gas has the added advantage of emitting almost no particulate matter or sulphur dioxide when used as fuel. Other cost-effective approaches to emissions control include combustion modifications. These can reduce NOx emissions by up to 50 % at reasonable cost. Flue gas treatment systems can achieve greater emissions reductions, but at a much higher cost. New recovery boilers are designed to reduce the formation of NOx within the combustion process primarily as a result of the correct air register and geometrical design of the boiler.

4.16 Electrostatic Precipitators

Electrostatic precipitators (ESPs) are one of the most widely used highly efficient particulate pollution control equipments used mainly for the treatment of gaseous effluents at high flow rates (REHVA 2005). It removes particles from a flowing gaseous stream such as air using the force of an induced electrostatic charge. ESPs are filtration devices that minimally impede the flow of gases through the device, and can easily remove fine particulate matter such as dust and smoke from the air stream. Consequently electrostatic precipitators are widely used in thermal power plants, cement plants and pulp mills. Apart from a high efficiency, other advantages are related with the fact that this type of equipment has a considerable low payback time in industrial plants where the particulate recovered from the gases has commercial value and can be recycled within the industrial process itself or even sold to other industrial companies. Where Kraft pulp mills are concerned, an electrostatic precipitator or a set of these equipments, is used to achieve treatment of waste gases from recovery boilers by collecting the load of particulate which is mainly formed of sodium sulphate, a chemical compound that is recycled back to the production process. ESPs remove particles in much the same way that static electricity in clothing picks up small pieces of lint. Transformers are used to develop extremely high voltage drops between charging electrodes and collecting plates. The electrical field produced in the gas stream as it passes through the high voltage discharge introduces a charge on the particles, which is then attracted to the collecting plates. Periodically the collected dust is removed from the collecting plates by a hammer device striking the top of the plates (rapping) dislodging the particulate, which falls to a bottom hopper for removal. Electrostatic precipitators are often configured as a series of collecting plates to improve overall collection efficiency. Efficiencies exceeding 99 % can be achieved. In some applications water is used to remove the collected particulates. ESPs using this cleaning mechanism are referred to as "wet ESPs" and are often used to remove fumes such as sulphuric acid mist. ESP can be operated at high temperature and pressures, and its power requirement is low. For these reasons the electrostatic precipitation is often the preferred method of collection where high efficiency is required with small particles. In the electrostatic precipitation process the basic force which acts to separate the particles from the gas is electrostatic attraction. The particles are given an electrical charge by forcing them to pass through a corona, a region in which gaseous ions flow. The electrical field that forces the charged particles to the walls comes from electrodes maintained at high voltage in the center of the flow lane (Theodore 2008).

Electrostatic precipitators are a demonstrated control technique for reducing PM emissions from kraft recovery furnaces and lime kilns. The PM emissions from over 98 % of kraft recovery furnaces and approximately 10 % of kraft lime kilns are controlled with ESP's. Paper mills face some unique challenges when it comes to optimizing the performance of electrostatic precipitators. Resistivity, for example, is a key issue for power boilers fired by wood waste (bark burners) because often the ash is high in calcium. Carbon carryover (loss on ignition, LOI) and heavy inlet ash loading can also limit ESP performance. For recovery boilers, dust resistivity is typically not a problem, but collection is made difficult because the recovered chemical compounds tend to consist of very fine particles and the dust loading can also be relatively high, leading to significant suppression of inlet field current levels. Proper operating temperature, good gas-flow distribution, good mechanical alignment and optimized rapping are needed to comply with emission limits on a consistent basis.

Recovery boiler precipitators tend to suffer from corrosion of both the casing/shell and internal components, because the flue gas is high in acid and moisture content. Wet bottom precipitators are especially susceptible to this problem. For example, because of baffles between fields, there is typically little or no flow just above the liquor level. In these locations, shell wall temperatures fall below the acid dew point, and sometimes even below the moisture dew point. Corrosion occurs in these areas and other spots where flow and temperature are both low. Ensuring that flue gas and shell temperatures are well above the acid dew point is the key to minimizing corrosion. To do that, it's necessary to find and fix sources of air in-leakage (cold outside air getting in), and maintain good insulation. In some cases, it may be necessary to add heat tracing for parts of the shell.

Because of these challenges, it's not uncommon for a paper mill to meet emission requirements with relative ease, yet still have trouble complying with opacity limits. This is especially prevalent with recovery boilers. Routinely meeting emission limits requires optimizing boiler operation (not exceeding boiler firing by more than 5–10 % of design) and gas flow distribution into and out of the precipitator. It's also necessary to perform regular ESP maintenance, including minimizing air in-leakage.

ESPs are very efficient devices for collecting ultrafine particles (<0.5 Zm), providing the particles have the ability to agglomerate, as e.g. recovery boiler dust (European Commission 2013). In kraft pulp recovery boilers, the particle size allows a good separation efficiency of the ESP. No aerosols are formed during combustion. There are a number of special considerations to be addressed when designing and operating an ESP for use after the recovery boilers. Some of the key recommendations are:

- Avoid flat surfaces in the gas path from the boiler to the ESP to prevent dust build-up; each gas path should be designed to allow a portion of the gas cleaning system to be taken out of service for maintenance while the boiler is operating at a reduced load (i.e. design for 70 % of total flow through one ESP system);
- With an increase in DS in the liquor, there is often an increase in the dust loading to the ESP
- The pH of the dust must be kept above 8.5 to avoid sticky dust that will be difficult to remove from surfaces
- Gas flow distribution into each ESP must be kept as stable as possible (standard deviation of the gas flow after the first collection field should be 20 % or less)
- Due to the difficulties in removing collected dust from the collecting electrodes the electrode height, length and total area of collecting surface per rapper must be sized appropriately
- The dust removal system from the bottom of the ESP must be very robust, reliable, efficient and must not contribute to dust re-entrainment.

The performance of existing ESP installations can often be improved without the need for total replacement thereby limiting costs. Improvements of ESPs can be done by fitting more modern electrodes, installing automatic voltage controllers or upgrade of the rapping systems. In addition, it may be possible to improve the gas passage through the ESP (improved gas flow distribution) or add supplementary stages. The performance of an existing ESP can be improved through improving the alignment of emitting electrodes with the collecting electrodes, eliminate gas sneakage around the electrodes, improve the collecting plate cleaning and ensure that electrical power supply is optimised. The latter may need to have the T/R set and controls changed. However, there are times when the increase in gas and dust load to the ESP or reduced allowable emissions from the plant are such that making changes to power supplies and controls will not be sufficient. In these cases, the existing ESP size would need to be increased. Only after a thorough evaluation of the existing ESP size, past performance and new performance requirements, the determination of the correct approach to upgrade the existing plant be determined.

The black liquor composition may change the ESP performance. The dust may adhere stronger to the collecting plate. Cleaning the electrodes may need adjustment of the rapping. Modern control systems can detect this and alter the rapping for optimal performance. Also the electrical power input will adapt to such a changing situation.

The size and electrical power consumption of ESPs increases exponentially with the decreasing of clean gas dust content. An ESP depends on defined raw gas conditions, such as temperature and humidity, for optimum operation. The lifetime of an ESP can be several decades, providing all recommended maintenance is properly carried out. Some parts, such as hammers and bearings, need regular replacement after a few years of operation as part of routine maintenance.

Many times the ESP performance is affected by dust composition, gas flow distribution and gas volume, sneakage around the charging/collection systems, improper rapping system design, not having advanced power supplies and controls, and general and poor maintenance of the ESP over time. Keeping the internals of the ESP clean, properly aligned and powered with the latest type of control system is needed to achieve best performance. Routine inspections and scheduled maintenance of the ESP internals will result in reliable operation.

Monitoring the power input to each section of the ESP and reacting to large variations will help to keep the unit performing well: the dust collection efficiency of the ESP is maximised when the charging of the dust particles is optimised and the T/Rs that are used to convert the plant alternating current to high voltage direct current are operating at peak levels. Closely monitoring the secondary voltage (kV), current (mA) and the sparks per minute (spark rate) from each T/R and addressing variations by boiler operation are needed to achieve the best possible collection of the dust. Higher levels of secondary current and lower amounts of sparking are key factors in maximising ESP collection efficiency. For the overall performance of ESPs, it is important to avoid CO trips. Because of their high efficiency, low pressure loss, high availability and energy efficiency, electrostatic precipitators became successfully established for dust collection from recovery boiler exhaust gas. The major disadvantages of ESPs are their decreased efficiency with an insulating layer and the possible build-up of material on the collection plates. No bag filters applications for recovery boilers have been reported. The nature of the dust and flue-gas composition from recovery boilers are not well suited for the bag materials used in fabric filters. The gas temperature and moisture content are higher than most filter bags can accept. The dust is small in size and is often very sticky. This type of dust composition would be difficult to clean from the bags resulting in a very high pressure drop across the filter. Boiler upset conditions could also result in bag damage that would require an outage to repair (Stubenvoll et al. 2007; EIPPCB 2011).

The ESP's used to control PM emissions from kraft recovery furnaces and lime kilns are generally classified as plate-wire ESP's. In plate-wire ESP's, the flue gas flows between parallel sheet metal plates and high voltage electrodes. The flue gas passes between collecting plates into a field of ions that have been negatively charged by the high-voltage electrodes located between the plates. Each paired set of electrodes and plates forms a separate electrostatic field within the ESP. Electrostatic precipitators used to control PM emissions from kraft recovery furnaces typically have two parallel precipitator chambers (i.e., flue gas passages) with three or four electrostatic fields per chamber. Lime kiln ESP's typically have one chamber with two or three electrostatic fields. As the flue gas passes through each electrostatic field, the particles suspended in the flue gas are bombarded by the ions, imparting a negative charge to the particles. The negatively charged particles then migrate towards the positively charged or grounded "collecting" plates, where the particles transfer a portion of their charge, depending upon their resistivity. The particles are kept on the collecting plates by the electrostatic field and the remaining charge. At periodic intervals, the collection plates are knocked and the accumulated PM falls into the bottom of the ESP. The recovered PM is subsequently recycled to the black liquor in recovery furnace applications or, in lime kiln applications, fed back to the kiln. The ESP's used on recovery furnaces may be designed with either a wet or dry bottom. In wet-bottom ESP's, the collected PM falls directly into a pool of liquid, which may be black liquor or water, in the bottom of the ESP. In dry-bottom ESP's, the collected PM falls to the (dry) bottom of the ESP and is transferred from the ESP bottom to a mix tank (containing black liquor) via drag-chain or screw conveyors.

Electrostatic precipitators of many mills achieve dust emissions from reburning lime kilns of between 5 and 25 mg/Nm^3 determined as annual average value (at 6 % O_2) or 0.02 kg dust/ADt. An example for achieved dust emissions over a complete year show that the dust emissions from the lime kiln are <25 mg/Nm^3 as a daily average (dry gas, 273 K, 5–6 % O_2), or less than 20 mg/Nm^3 as annual average. The data are taken from the on-line transfer of emission data of the competent authority. In a 1500 ADt/d kraft mill, the investment required for an electrostatic precipitator at the lime kiln is EUR 5 million – 6 million. The operating costs are less than EUR 0.3 million/year (European Commission 2013).

4.17 Installation of Scrubbers on Recovery Boiler

The recovery boiler can be equipped with a flue gas scrubber in order to reduce the emissions of sulphur 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, SO_2 and particulates are removed. Scrubbing takes places at a pH of 6–7. The pH value is controlled with addition of sodium hydroxide, weak liquor or oxidised white liquor. SO_2 reacts with the scrubbing liquor and Na_2SO_3 and also some Na_2SO_4

is formed. TRS in the form of H_2S can be removed together with SO_2. However, to remove hydrogen sulphide from the flue gases, a high pH of the scrubbing liquor would be required. At such a high pH, also carbon dioxide would 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 also existing boilers can be equipped with scrubbers. Recovery boilers burning high dry solids black liquor normally give rise to low sulphur emission which makes the installation of scrubber less interesting.

The removal efficiency for SO_2 is typically >90 %. A scrubber on the recovery boiler can reduce the sulphur emissions from 0.5 to 2 kg/Adt down to 0.1–0.3 kg S/ADt or concentrations from 50 to 200 mg/Nm^3 down to 10–50 mg/Nm^3. Continuous SO_2 measurement prior to and after the scrubber is needed to control the operation of the scrubber.

By introduction of fresh water 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 oxidised white liquor, weak liquor or sodium hydroxide, which can increase the capacity demands on the recovery department.

Wet scrubbers are used at about one third of the recovery boilers. However, if utilized, the reason is often also heat recovery. The removal efficiency of wet scrubbers for SO_2 is typically >90 %. According to the data gathered, the same performance for SO_2 reduction can be achieved by using high dry solid content firing and by using wet scrubbing of the flue-gas.

For those mills that even though running the recovery boiler at high dry solid content have higher SO_2 emissions (e.g. because of boiler overload), a scrubber can be a measure to reduce these emissions.

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

Benefits of this technology are reduction of SO_2 emissions; heat recovery; dust removal in some cases. In pulp mills that run the recovery boiler with a high DS content, the SO_2 emission can be substantially reduced and for such mills, there is not much of a need to install scrubbers. The internal energy situation of the mill might or might not motivate warm water production in the scrubber. In a modern kraft recovery boiler, especially if it operates on high DS, the H2S is normally not a problem that needs scrubbing to resolve. Scrubbers can also be used as a second part of a two-stage dust removal facility (ESPs and wet scrubbers). Scrubbers have been installed on numerous recovery boilers in Europe.

4.18 Increase in the Dry Solids 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 oxidised and generate heat. In a conventional recovery boiler, there is an oxidizing zone in the upper part and a reducing part 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 up-wards). Emissions generated from the recovery boiler mainly consist of particulates, nitrogen oxides and sulphur dioxide. The emission levels are kept low by optimising the combustion parameters – temperature, air supply, black liquor dry solids content and the chemical balance. The objective of improved evaporation is to obtain as high content of dry solids (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 obtained by installing a superconcentrator. However, the achievable DS-content depends on the type of wood. A target for optimal dry solid content of thick liquor in a balanced mill could be 72–73 % after evaporation but measured before the recovery boiler mixer.

The most effective way to reduce both TRS and sulphur dioxide emissions from kraft pulp mills is to run the recovery boiler with high dry solid content. The sulphur content of CNCG and the fuel oil burnt in the recovery boiler are less significant for the reduction of sulphur dioxide emissions.

Sulphur dioxide emissions are formed mainly through the oxidation of hydrogen sulphide and carbonyl sulphide in the lower furnace. The major source of gaseous sulphur emissions is the black liquor and the sulphur content in additional fired streams such as CNCG. The emission levels are kept low by operating the boiler with high black liquor dry solids content (higher temperature) and by optimising the combustion parameters such as air supply and mixing of air and fuel. The emission of sulphur from the recovery boiler is affected by the following operating variables:

- Temperature in the different zones which is affected by the dry solids content (heating value) of the strong black liquor and the amount of combustion air. With higher DS feedstock, the combustion temperature increases and causes more sodium to be vaporized. This then takes up the sulphur dioxide and form sodium sulphate, thus reducing sulphur dioxide emissions from the recovery boiler. On the other hand, the fact that more sulphur is driven of in the evaporation when the dry solids content of the black liquor is raised, could reduce the sulphur reaching the recovery boiler if the sulphur-containing odorous gases from evaporation are not burnt in the recovery boiler. However, at high temperature, emission of NOx may increase.
- At higher sulphidity levels, the release of sodium in the furnace in relation to the sulphur amount may not be enough to bind all the sulphur emitted and thus a

share of the sulphur may leave the furnace as sulphur dioxide instead of sodium sulphate. High dry solids contents of the black liquor may compensate this effect.

- Excess air supply, primary air temperature and distribution of combustion air.
- Operating a recovery boiler in an overloaded mode has a harmful effect on the emission characteristics of sulphur dioxide. The load of the furnace is directly proportional to the temperature in the furnace. When the load of the furnace is changed, the temperature changes accordingly. In some boilers, the sulphur dioxide emissions are sensitive to changes in load i.e. sulphur dioxide emissions may change due to the temperature changes in the furnace. Sulphur dioxide emissions may also increase when the boiler load is reduced. Sulphur dioxide emissions from other boilers with very high DS do not react to changes in the boiler load.

Increasing the firing concentration of the black liquor has been shown to be feasible and to increase the capacity of the boiler (AFPA 1988; EPA, NCASI 1995; Hyoty and Ojala 1988; Huber et al. 1995; Ibach 1995). Several boilers fire black liquor at concentrations between 75 and 79 %. Many evaporator installations since about 1989 have been designed to produce 80 % concentration black liquor (McCubbin 1996). Huber et al. (1995) described a project that resulted in increasing the concentration from 68 to 75 % of the liquor fired in the boiler at Pope & Talbot’s Halsey, Ore., mill. This increased the boiler capacity from 806 tpd of black liquor solids to 1020 tpd (approximately 16 % increase). It was later on reported, that the boiler was successfully fired at up to 1180 tpd, representing an increase of 28 % in capacity. This project also included the installation of a liquor heat treatment system, which reduces the calorific value of the liquor by about 5 %. Some of the increase in capacity can be attributed to this. Lefebvre and Santyr (1989) stated that calculations using Combustion Engineering Inc. (ABB) boiler simulation software indicate that where the capacity of a boiler is limited by plugging, increased solids throughput could be achieved by increasing the liquor firing consistency. Increase of several percent in capacity due to reduced temperatures in the boiler bank and reduced gas flow. The higher flame temperatures resulting from the high-concentration liquors increases heat transfer to the water walls in the lower furnace, which leads to lower temperatures in the critical boiler bank, thus reducing the tendency to plug the passages within the boiler (AFPA 1988). Imelainen et al. (1989) reported modifications to a recovery boiler at the Kemi mill in Finland, where they attributed an increase of 15 % in boiler capacity to raising liquor firing consistency from the low 60 % to the low 70 %. It was found that increasing consistency from 65 to 75 % reduced sulphur dioxide emissions substantially and increased the thermal efficiency from 55 to 60 % while improving reduction efficiency from 95 to 97 %. The same change in firing conditions increased the dust emissions from the boiler itself by 30 %, but resulted in lower stack particulate emissions due to an improvement in the electrostatic precipitator’s performance resulting from the lower gas flows and temperatures. Hyoty and Ojala (1988) described three years’ experience of operating a “super concentrator” to evaporate black liquor to 78–82 % and fire it in a recovery boiler at a mill in Pori, Finland. The authors concluded that boiler operations had improved in a number of ways, with the only difficulty being the extra operator attention required by the high-solids evaporator. It was reported that the effective increase in boiler capacity was 15 % when increasing firing consistency from 65 to 80 %. The boiler reportedly fired routinely with 78 % consistency liquor, since this provides sufficient capacity for the mill's requirements. Increasing the black liquor firing consistency generally involves installing an additional black liquor evaporator, usually known as a concentrator, to raise the concentration to the desired level, which may be up to 80 % dry solids. In most cases, the viscosity of the thick black liquor is the limiting factor. This can be readily reduced by heat treatment, but the capital cost of the necessary equipment (typically a few million dollars) may be unacceptable. Several mills use a heat treatment process to lower the viscosity of high-concentration black liquor. Ryham and Nikkanen (1992) described a system where the black liquor was heated to 180 °C near the end of the evaporator set, permanently reducing viscosity by a factor of about 5 (Ryham and Nikkanen 1992). The absolute reduction was most pronounced at high-liquor concentrations (65–80 %). The equipment used to treat the liquor is effectively a multiflash evaporator, and it raised the concentration of the liquor by about 5 %. It also caused sufficient emission of reduced sulphur gases to replace 12 % of the fuel burned in the mill's lime kiln. This corresponds to about a 4 % drop in the calorific value of the black liquor, which in itself increases the boiler's capacity to burn black liquor solids. Ryham and Nikkanen (1992) reported an improvement in reduction efficiency from 93 to 96 %. This is marginally beneficial to recovery boiler capacity. Huber et al. (1995) described a comparable installation at the Halsey, Ore., mill. Heating value of the black liquor was lowered by 4 to 5 % by the heat treatment, due to evolution of sulphur gases that are burned in the lime kiln. The increase in boiler capacity was 28 %, as mentioned above. This was attributed to a combination of lowered calorific value of the black liquor, increased liquor firing concentration (from 68 to 75 %+), and a cleaner burning liquor.

The emission of total reduced sulphur (TRS) from the recovery boiler is influenced by almost the same operating variables as the sulphur dioxide emissions.

- Due to firing high dry solid content black liquor, there is enough sodium in the flue-gases to bind almost all sulphur formed in black liquor combustion. Sulphur emissions are found to be extremely low during full load and stable operated boilers. If there is enough sodium to bind all the sulphur, virtually there is no sulphur dioxide emissions (Tamminen et al. 2002).
- The load of the furnace is directly proportional to the temperature in the furnace. Operating a recovery boiler in an overloaded mode may have a negative effect on the emissions characteristics, particularly the quantity of hydrogen sulphide produced. Rapid changes in the operation mode may generate some momentary TRS peaks. TRS emissions from boilers with very high dry solid content do not react to changes in the boiler load.
- The main controlling factor for the TRS emissions from recovery boiler furnace is mixing of oxygen and sulphur containing gases. If the gases are well mixed they are converted to sulphur dioxide. Modern air systems help in obtaining sufficient mixing.

Increasing dry solids **r**educes sulphur emissions but increases NOX emissions if no counter measure is taken. Running recovery boilers at high dry solids and high furnace temperatures maximises the electricity production from the boilers (high pressures and temperatures). The reduction of sulphur emissions by high DS content increases the emissions of particulates prior to flue-gas cleaning. To compensate for this, a more efficient and expensive electrostatic precipitator has to be installed. At very high DS content (DS >80 %) there is a significant release of sulphur compounds from the last evaporator stage, which have to be collected and incinerated.

The process can be applied at both new and existing kraft mills. A superconcentrator can be implemented as a separate phase also to existing evaporation plants. Viscosity problems can be handled with pressurised storage or heat treatment before the last concentrator. 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/d kraft pulp production the investment required for increased black liquor concentration from 63 % upward are as follows (European Commission 2013):

- concentration from 63 to 70 %, EUR 1.7 million – 2.0 million
- concentration from 63 to 75 %, EUR 3.5 million – 4.0 million
- concentration from 63 to 80 %, EUR 8.0 million – 9.0 million

Increasing the dry solids content does not increase operating costs, and indeed significant savings are possible. The measure increases the energy economy of the mill and leads to gains in recovery boiler capacity. Driving force for implementation are increased process efficiency. The Finnish recovery boilers are on average firing close to 80 % dry solids; Swedish recovery boilers are on average firing close to 70 % dry solids (FRBC 2010; Finnish BAT Report 1997).

4.19 Incineration of Odorous Gases in the Lime Kiln

Disposal of malodorous gases from the kraft process is a difficult waste stream problem in the Pulp and Paper industry. The human detection threshold is as low as 1 part per billion (ppb) for reduced sulphur gases (USEPA 1976). Non-condensible gases (NCG's) containing reduced sulphur gases are not only noxious but also very hazardous. NCG's are highly corrosive due to the sulphur compounds and chlorides with water vapor, and volatile enough to be explosive. Disposal of various NCG's in Pulp and Paper mills is always a concern if present and future environmental regulations are to be met. The primary sources of NCG's in a kraft mill are digesters, evaporators and turpentine recovery systems. Kraft mill odor can be attributed to four reduced sulphur gases namely:

Hydrogen Sulphide (H2S)
Methyl Mercaptan (CH_3SH)

Table 4.35 Typical noncondensable gas analysis by volume % of an NCG gas stream

Hydrogen sulphide	1.7
Methyl sulphide	2.1
Dimethyl sulphide	2.1
Dimethyl disulphide	1.7
Turpentine	0.1
Methanol	0.2
Water Vapor	6.0
Nitrogen	77.2
Oxygen	8.9

Based on Santos and Backlund (1992)

Dimethyl they Sulphide (CH_3SCH_3)
Dimethyl Disulphide (CH_3SSCH_3)

These gases are collectively referred to as total reduced sulphur (TRS) gases. Volatile organic compounds (VOC) other than those containing sulphur are also emitted during digester relief. Typical constituents are alcohols, terpenes, and phenols. Table 4.35 shows a typical analysis of an NCG gas stream.

Incineration (or thermal destruction) has been well recognized in the paper mill industry as the preferred method of disposal. Firing NCGs in the power or recovery boilers is often more troublesome because of high capital and maintenance costs plus, the increased emissions of sulphur dioxide in the stack.

Incineration of concentrated NCG is conducted in the lime kiln or in a separate NCG incinerator having sulphur dioxide -scrubber. The concentrated NCGs contain over 90 % of all TRS compounds generated in the cooking of pulp. Efficient odourous gas collection from all sources and effective treatment reduces sulphur emissions and annoying smell in the neighbourhood

High concentrated and low volume gases are produced in:

- Turpentine recovery system
- Continuous digester flash steam condensers
- Foul condensate storage tanks
- Evaporator non-condensable gas 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
- Storage tanks of white liquor in the recausticising 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 lime kiln 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 lime kiln is that no extra furnace is needed. Also, the sulphur in the gas can be absorbed in the lime, which decrease the emission of sulphur dioxide. However, only a limited amount of sulphur can be absorbed in the lime kiln by gaseous sodium forming sodium sulphate. The main sulphur absorbing compound is sodium carbonate in the lime mud. When this capacity is exhausted, sulphur dioxide is released. This effect is increased when malodorous NCGs are incinerated in a kiln. So, sulphur dioxide emissions are usually a clear function of the amount of malodorous gas flow. To reduce the formation of sulphur dioxide either the sulphur content in the fuel can be reduced or if malodorous NCGs are to be burnt in the lime kiln, sulphur compounds can be scrubbed out of these gases before burning in the lime kiln.

TRS-control can also decrease the malodorous constituents released in the wastewater treatment. An average 10–15 % of the fuel used in a lime kiln 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.

Investment costs of collection and incineration of both strong and weak gases are typically 4–5 MEuros at new mills and 5–8 MEuros at existing mills with a capacity of 1500 ADt/d (European Commission 2001). No major increase in operating cost, if the heat value of recovered methanol can be utilised. Otherwise, an increase of 0.3–0.5 MEuros/a is expected. The reduction of TRS emissions of the kraft mill is a major reason to implement this technique (Hupa 2005; EIPPCB 2011; Botnia Rauma 2009; FRBC 2010; DeMartini 2010; Malmström 2010; European Commission 2001).

Though the lime kiln is the first choice for most plants, but mill production can be affected by any downtime in the kiln. Potlatch Corporation at their Cypress Bend facility near McGehee, Arkansas realized that an alternative stand-by system was necessary to keep production at near 100 % and meet the strict environmental regulations. The modular incinerator concept can accommodate different high performance burners for different composition and volumes of waste streams. If there are space constraints, a modular incinerator can operate in different configurations (i.e vertically or horizontally). Modular systems allows future retrofit at minimal cost. A stand alone incinerator can reduce problems associated with incinerating NCG's in the lime kiln, power boiler or recovery boiler. Ringing problems in lime kilns have been attributed to incineration of concentrated NCG's. Corrosion problems in boiler tubes and reduction of boiler efficiency have been blamed on NCG firing. With more stringent environmental regulations requiring tighter closure of all industrial processes and pressure to reduce odorous emissions, stand alone incinerators become a more feasible and attractive means of NCG disposal in the pulp and paper industry.

4.20 Installation of Low NOx Technology in Auxiliary Boilers and the Lime Kiln

The formation of nitrogen oxide emissions from pulp mills is significantly more complicated than was perceived before. Detailed studies on the formation of nitrogen oxides in the burning of black liquor started in the 1990s. However, a complete picture of the cycle of nitrogen compounds at pulp mills has only been clarified now. In particular, the sodium cyanate (NaOCN) forming in the recovery boiler smelt and the ammonia generated through it in the chemical recovery cycle are the major factors, the importance of which has only been understood in the last few years. Nitrogen is mainly introduced into the mill with wood chips, but other nitrogen sources are also available, including defoamers, anti-scaling agents, chelating agents, etc. Their contribution has been considered to be negligible, but they may, however, have an effect on the black liquor nitrogen content in the future. The recycling of fibreline filtrates back to the recovery cycle in a mill with a high degree of closure may increase the nitrogen content of black liquor significantly (Telkkinen 1997). Raw wood material contains organic nitrogen compounds as natural constituents, typically 0.05–0.50 % of dry matter (Martius 1992; Nichols et al. 1993; Verveka et al. 1993; Kymäläinen 2001). In normal cooking, nitrogen compounds in the wood dissolve more or less completely in the alkaline cooking liquor and are transferred as part of the black liquor to the evaporation plant and further to the recovery boiler.

The lime kiln is an important part of the kraft process chemical recovery cycle. Emissions of NOx from the lime kiln are relatively low. They are influenced by the following parameters:

- Composition of materials fed to the kiln
- Fuel choice
- Chemical reactions that accompany lime mud calcinations
- Choice of external control approaches for particulate emissions

Combustion process modifications may be useful, but are limited by site-specific considerations and product quality impact.

Though the mechanisms differ, NOx produced in the kraft lime kiln originates from the combustion of fossil fuels, such as natural gas and residual fuel oil. The range of emissions is wide, and data are equivocal as to whether gas or oil is associated with the greater level. The introduction of other fuels and reduced sulphur compound bearing process gas streams such as stripper off-gases (SOGs), which are relatively rich in nitrogen content, increases the potential. Combustion modifications are the best prospect for altering NOx emissions. The opportunities are extremely limited, however, due to the temperature and combustion conditions that must be sustained to efficiently produce an end product (calcium oxide) of consistently acceptable quality. The NOx control strategies for each kiln have to be evaluated on a case-by-case basis since mechanisms of formation and control are not well understood (NESCAUM 2005). To illustrate, techniques to minimize the hot end temperatures in gas-fired kilns, while potentially helpful in reducing NOx emissions, must be balanced with the simultaneous need to address emission levels of total reduced sulphur compounds and to sustain the necessary calcining capacity. Reducing available oxygen in the kiln combustion zone may be useful for NOx reduction in oil-fired kilns, but effects on emissions of carbon monoxide and TRS emissions would have to be considered. Whatever combustion modifications are made may be limited by kiln configuration and geometry, and also by impacts on process performance, stability, and control.

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, sulphur dioxide and NOX emissions. Coal and lignite suit well to be burned as major or support fuel in fluidised bed systems, which by careful operation control promotes low NOx formation. In conventional oil or natural gas fuelled boilers, the burners feeding the fuel-air mixture, must apply designs that maintain low NOx 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 NOx 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 NOx combustion. Some air may still be fed, if necessary above the main flame area to complete the fuel combustion. The reason of the multi-phase 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 NOx formation; the flame temperature is lower than in conventional burners which further decreases NOX formation. Part of the NOx 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 NOx burners can be used both in the new and existing boilers. When powdered solid fuels are used it is important that they are pre-dried if they have high humidity to support fast and efficient burning. It is also required that the burning air is preheated to assure quick ignition and complete burning. Generally, emissions vary with the fuel. In comparison to conventional burners with 250–500 mg/MJ NOx emissions, the low NOx burners can reach 120–140 mg/MJ level in stack emissions.

With online NOx meters, emission monitoring can be carried out. Also oxygen meters can help to determine that low NOx burning conditions are maintained. Low NOx 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 MEuros. No major increase in the operating costs is anticipated. Low NOx burners are mainly used to reduce NOx emissions from auxiliary boilers (Rentz et al. 1996; Pöyry 1997, Finnish BAT Report 1997).

4.21 Selective Non-Catalytic Reduction on Bark Boilers

In Selective Non-Catalytic Reduction (SNCR) systems, ammonia or urea is injected into the furnace within a suitable temperature window. Emissions of NOX can be reduced by 30–70 % by the reaction between NO and the reducing agent to form nitrogen and water. The most common reagents used in SNCR processes are given below:

- Anhydrous ammonia
- Aqueuos ammonia
- Urea solution

SNCR is a simple process, referred to as "thermal deNO$_x$", and involves the reduction of NO$_x$ to nitrogen in the presence of oxygen by reaction with amine-based reagents, either ammonia (NH_3) or urea, $CO(NH_2)_2$ at 1073–1273 K, the higher temperature being needed for urea. Exxon developed the SNCR process and first applied it in 1974 (Lyon 1987).

With NH_3 as the reagent the reaction scheme is shown below (Lyon 1979):

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O$$

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$$

With urea as the reagent the reaction scheme is as follows:

$$H_2NCONH_2 + 2NO + \frac{1}{2}O_2 \rightarrow 2N_2 + CO_2 + H_2O$$

The reagent ammonia or urea can be injected directly into the fluidized bed or riser. The SNCR process efficiency depends upon the following (Teixeira et al. 1991):

- Temperature
- Reagent/flue gas mixing
- Reagent/NO_X ratio
- Reaction time

SNCR systems reduce NO_x emissions by 30–90 % but the performance is highly variable for different applications. A typical SNCR system involves reagent storage, multi-level reagent-injection equipment, and associated control instrumentation.

The SNCR reagent storage and handling systems are similar to those for SCR systems. However, because of higher stoichiometric ratios required at equivalent efficiency, both ammonia and urea SNCR processes require larger quantities of reagent than SCR systems to obtain similar NO_x reductions. The capital cost of SNCR is low compared to that of SCR systems since there is no catalyst, and overall operating costs are similar (Mahmoudi et al. 2010). The addition of aluminium-based catalysts has been suggested for the full and rapid decomposition of urea.

In the SNCR process, it is the ammonia molecule that is the active reducing agent. When using urea solution in such a deNOX process, the urea will be first converted into ammonia prior to the deNOX process. The dominating reaction in the SNCR processes in combustion processes where NO is the main NOX species is:

$$4NO + 4NH_3 + O_2 f 4N_2 + 6H_2O$$

In the more efficient SCR process about 1 mole of ammonia is required per mole of NO_X reduced or about 0.5 mole urea per mole NO_X reduced. The SNCR process is not as efficient as SCR when it comes to reagent utilisation. In this process, the reagents needs to be dosed in an over-stoichiometric ratio. For SNCR it can be in the range of 1.5–2 (or even higher in some cases). The approximated reagent consumption for SCR and SNCR process is:

SCR: 1 kg NOX reduction require 0.37 kg NH_3 or 0.653 kg urea.
SNCR: 1 kg NOX reduction require 1.2–1.9 kg NH_3 or 2.2–3.3 kg urea.

The temperature window for efficient SNCR operation is typically between 800 and 1050 °C. When the reaction temperature increases over 1000 °C, the NOX removal rate decreases due to thermal decomposition of ammonia. Below 800 °C, the NOX reduction rate decreases and ammonia slip may increase. The longer the reagent is in the optimum temperature window, the better the NOX reduction. Residence times in excess of one second yield optimum NOX reductions. Ammonia slip from the SNCR systems occurs either from injection at temperatures too low for effective reaction with NOX or from over-injection of reagent. Controlling ammonia slip in SNCR systems is difficult since there is no opportunity for effective feedback to control reagent injection. Another difficulty is that the reagent should be placed where it is most effective and the NOX distribution varies within the boiler cross section. Distribution of the reagent needs to be particularly controlled in larger boilers because of the long distance required to cover the cross-section of the boiler. Multiple points of injection are commonly used to follow the temperature changes caused by boiler load changes. In well controlled SNCR systems, ammonia emissions are in the range of 1–10 mg/Nm^3.

Injected urea or ammonia does not react completely but a small share of the reagent escapes in the flue-gas. The benefit of reduced NO should be weight against increased ammonia emissions and ammonia slip controlled and kept as low as possible. Depending on the stoichiometry the urea is added, a slight increase of ammonia (slip) may be determined but measurements demonstrate the risk to be marginal. A potential danger is unreacted ammonia combining with SO_3 to form ammonium bisulphate. Ammonium bisulphate will precipitate at air heater operating temperatures and can ultimately lead to air heater fouling and plugging. If not properly controlled, there is a certain risk that an SNCR process may produce nitrous oxide, which contributes to the greenhouse effect. However, nitrous oxide emissions are more likely to occur at coal-fired boilers than at biomass-fired ones. Carbon dioxide emissions associated with the use of urea and ammonia for NOX reduction are relatively small to negligible compared to overall generation of carbon dioxide in pulp and paper production; on the other hand, reduction of NOX emissions is required for health reasons and to protect environment from adverse effects such as:

- Euthrophication,
- Acidification
- Ozone formation

For SNCR, a reduction of 30–70 % is reported (European Commission 2013). The result of the application of SNCR is very sensitive to variations in the operational conditions of the boiler and urea/ammonia dosing needs to be controlled permanently. Continuous NOX measurement should be carried out and experience shows reliable results. The total NOX reduction achievable in a bark boiler is about 30–50 % by changing the combustions techniques and/or by applying an SCNR process. The NOX emissions would then amount to 40–60 mg/MJ equal to about 100–200 mg/Nm^3. Achieved emission data for SNCR applications in fluidised bed boilers can also be seen in Table 4.36.

Bark boilers give relatively low NOx emissions because of the low combustion temperature. When only bark is fired, emissions are typically 70–100 mg NOx/MJ and when oil is used in the bark boiler, NOx increases to about 100–150 mg NOx/MJ. NOx formation is affected by excess oxygen and should be avoided. Too low excess oxygen increases the risk for emissions of carbon monoxide and VOC. Primary NO is formed in furnaces either through reaction with nitrogen in air (thermal NO)

Table 4.36 NOx emission from fluidised bed boilers of paper mills using primary and/or secondary measures for NO_X reduction

Rated thermal input (MW)	Year of commissioning	Fuels	Flue gas cleaning system	NOX (mg/Nm^3)	CO (mg/Nm^3)	O_2 (%)	Observation
48	1994	Bark, sludge, paper, waste wood	Primary measures	90–220 (DAV)	3–20 (DAV)	11	Corg <2 mg/Nm^3
				142–187 (MAV)	4–9 (MAV)		
				165 (YAV)	6.4 (YAV)		
4.8	2003	Waste wood, rejects, sludge	Primary measures, SNCR	161–171 (YAV)	2.3–2.8 (YAV)	11	Corg <1 mg/Nm^3

Based on European Commission (2013)

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 oxidised to NO_2. In the SNCR process, NO is reduced by urea to nitrogen, carbon dioxide and water according to the reaction

$$2\mathrm{NO}+\left(\mathrm{NH}_2\right)2\mathrm{CO}+½\mathrm{O}_2 \rightarrow \mathrm{N}_2+\mathrm{CO}_2+2\mathrm{H}_2\mathrm{O}.\ \text{The reaction occurs around } 1{,}000\,°\mathrm{C}.$$

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 NOx reduction to about 40 %. The total NOx-reduction achievable in a bark boiler is about 30–50 % by making change in the combustions techniques and/or by applying an SCNR process. The NOx emissions would then amount to 40–60 mg/MJ equal to about 100–200 mg/Nm^3. Emissions of gaseous sulphur are low or about 10–20 mg/MJ when burning bark. Continuous NOx 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 NOx reductions achieved by these techniques. The process can be a potential source of emission of N_2O or ammonia but measurements demonstrate the risk to be marginal.

Full scale trials both with urea and ammonia have been carried out in Sweden. The trials showed NOx emission reductions of 10.30 %, with one test up to 60 %. The efficiency depends on many factors, e.g. 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 for adding SNCR to the bark boiler for a bleached kraft mill with a production capacity of 250,000 and 500,000 t/a amount to 690,000 Euros and 1.15 MEuros respectively (European Commission 2001). 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 per kg NOx removed.

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

4.22 Over Fire Air Technique on Recovery Boilers

The formation of NOx in the Kraft recovery boiler is lower as compared to other furnaces because it operates with a reducing atmosphere in the bottom. Modifications to the air feed system have been found successful with respect to NOx reductions. By limiting the amount of air in the combustion zone, thermal NOx by fixation of nitrogen in the combustion air can be reduced. A reduced NOx formation can be obtained in a kraft recovery boiler by modification of the air feed system such as introducing a fourth air inlet in the upper part of the boiler (European Commission 2001). The reduction of NOx emissions attributable to the use of this technique is variable. It depends on the boiler type and design and the method of Over Fire air (OFA) application, and will normally be 10–25 %.

OFA is a NOx reduction technique that removes a portion of the combustion air from the burner wind box. This air is introduced to OFA ports located above the burners. This technique provides an additional layer of air staging to the furnace zone. When the diverted air is introduced above the burners, the combustion is completed and the remaining CO is burned out. OFA has been incorporated in multiburner units since the 1970s. Older OFA port designs are not as effective as current generation of OFA ports. In some cases, original OFA ports have been removed because they were ineffective or caused boiler performance and maintenance issues. Using CFD modeling, current generation OFA systems are found to be capable of 25 % NOx reduction with minimal impact to the unit operation. An alternative to dedicated OFA ports is a tuning technique known as burners out of service (BOOS). BOOS is implemented by taking one burner or row of burners out of service. Out-of-service burners act as OFA ports by permitting the remaining burners to run lean. The remaining required combustion air is supplied through the BOOS to complete combustion. BOOS reduces boiler efficiency by increasing the excess oxygen requirement by about 1 %.

Furnace OFA requires combustion air to be separated into primary and secondary air to achieve complete burnout and to formation of nitrogen rather than NO_X. The primary air (70–90 %) is mixed with the fuel producing a relatively low-temperature, oxygen deficient, fuel-rich zone and moderate amounts of fuel NO_X are formed. The secondary (10–30 %) combustion air is injected above the combustion zone. The relatively low-temperature secondary-stage limits the production of thermal NO_X. The location of the injection ports and mixing of overfire air are critical to maintain efficient combustion.

B&W pioneered the development and application of NOx ports and air staging as a NOx emissions control technique. Combined with B&W's other low NOx technologies, such as burners and selective catalytic reduction systems, overfire air systems are part of an overall NOx reduction strategy. Their combustion and OFA systems can be installed on all wall-fired and corner-fired steam generators. Air staging involves removing a portion of the air from the burners to reduce oxygen availability early in the combustion process and reintroducing it later in the combustion process. Often the physical arrangement dictates replacing the staged air through ports located above the combustion zone; hence the name OFA is commonly applied to such systems. The layout of a combustion system and furnace, however, may necessitate supplying staged air at the same elevation or below the burner zone, such that OFA is something of a misnomer. OFA is used here, in its generic sense, to refer to any air staged system. The ports through which the OFA is injected are called OFA ports or NOx ports.

It is applicable to both existing and new mills. The achieved NOx-reduction appears to be different from recovery boiler to recovery boiler. Following experiences have been reported in some Swedish kraft pulp mills (European Commission 2001):

1. Installation and use of OFA-technique on an existing recovery boiler and operation since 1990: 30 % NOx-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 % NOx reduction achieved and in operation since the beginning of 1997.
4. First new recovery boiler with OFA technique in 1996.

The reduction of NOx 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 for modifying the air introduction to the recovery for a bleached kraft mill with a production capacity of 250,000 and 500,000 t/a amount to 1.7 MEuros and 2.3 MEuros respectively (European Commission 2001). The investment costs include new air inlets to the recovery boiler, instrumentation, pipes and fans. There is no change in operating costs.

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

4.23 Installation of Improved Washing and Filtration of Lime Mud in Recausticizing

The recausticizing plant is a very important part of chemical recovery at the pulp mill. It uses dissolved smelt from the recovery boiler as a raw material and consumes lime to produce white liquor, which is an active chemical used in pulping. It also produces lime mud, which mainly consists of precipitated calcium carbonate particles, as a byproduct. The purpose of the lime reburning process is to convert the lime mud back into reburned lime for reuse in the causticizing process. The primary method used for the required high temperature treatment of the lime mud has been, and is still today even, a rotary lime kiln (Mehra 1979; Schroderus et al. 2000). The lime mud recovered from the white liquor clarification, which is the last stage in the causticizing process, contains substantial amounts of residual white liquor and therefore also large quantities of sodium hydroxide and sodium sulphide. These compounds must be removed from the mud because excessive amounts of sodium and/or sulphide in the mud will impair the operation of the kiln process. According to Prakash and Murray (1973), Steen and Stijnen (1984), the amount of sodium sulphide fed into the kiln is also directly related to the TRS emissions. Furthermore, according to Tran and Barham (1991) and Tran et al. (1993), ring formation in the kiln is associated with a high residual sodium content of the mud. Furthermore, these sodium compounds are valuable chemicals, and need to be recycled back to the process. In order to avoid these problems, the lime mud must be washed and dewatered before it is fed into the kiln. Efficient washing and filtration of the lime mud reduces the concentration of sodium sulphide in the lime mud, thus reducing the formation of hydrogen sulphide entering the kiln during the reburning process. Insufficient lime mud dry solids content and purity may also cause hydrogen sulphide formation. With modern LMD-filters a TRS content of 10 ppm can easily be achieved. Vacuum filters are mainly used for lime mud washing. Lime is used to causticise green liquor ($Na_2S + Na_2CO_3$) into white liquor ($Na_2S + NaOH$). After causticising, lime mud ($CaCO_3$) is formed. Normally lime mud is recycled in a lime kiln, where lime mud is reburnt and new lime is created. Before the lime is sent to the kiln it must be washed in order to remove residual sodium hydroxide, sodium sulphide and other sodium salts. The equipment used for lime mud washing are usually press filters. Single-stage lime mud washing in pressure filters are dominant (Arpalahti et al. 2000).

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 sodium sulphide in the lime mud through both washing and oxidation. Sodium sulphide is oxidized to sodium thiosulphate by passing air through the mud mat on the filter. The lower concentration of sodium sulphide in the lime mud reduces the formation of hydrogen sulphide in the lime kiln during the mud drying process. Improved washing of lime mud has been practiced since the late 1980s in kraft pulp mills. Monitoring of residual sodium hydroxide is required to avoid plugging of the lime kiln (SEPA-Report 4713-2 1997b).

Improved lime mud washing and filtration (LMD-filter) can reduce the residual content of white liquor in the mud from 100 mg/l to 0–30 mg/l in modern filters. The lime mud dryness can be increased to 70–80 %. In addition to energy savings the operation of the kiln becomes more stable. The LMD-Filter keeps the remaining sodium content in the lime mud at a low level, which also prevents process disturbancies like ring formation. Operational data Improved washing of lime mud is common practice in pulp mills in Europe. Monitoring of residual sodium hydroxide is required to avoid the damming of the lime kiln. No specific data concerning the effectiveness of this measure have been provided.

The main achieved environmental performance is possible reduction of hydrogen sulphide in the lime kiln, which depends mainly on the availability of sodium in the lime and the sulphur content of all fuels fed to the lime kiln. At the lowest sulphur input a small reduction can be achieved but with higher sulphur inputs the effect can be non-existent or detrimental. If washed to a too low sodium content, the emissions of TRS and also particulate emissions from the lime kiln tend to increase. Improved washing of lime mud has been practiced in several pulp mills in Europe. Investment costs are typically 1–1.5 MEuros (European Commission 2001). Driving force for implementing this technique is the reduction of hydrogen sulphide (TRS) and odours from the flue gases of the lime kiln (SEPA-Report 4713-2 1997b).

4.24 Technologies That can Help Achieve Practical Minimum Energy Consumption

Current pulp and paper facilities in many countries are nearing the end of their operating life and will need to be replaced over the next 10–15 years. This presents an excellent opportunity for new technology deployment to have an impact on energy savings in the sector in the medium term. This section describes few technologies which can help achieve minimum energy consumption.

4.24.1 Impulse Technology for Dewatering of Paper

Impulse technology is a high-intensity web consolidation technique in which water is removed from a wet paper web by the combined action of mechanical pressure and intense heat. Impulse technology implements the positive effect of increased web temperature on both dewatering rate and web consolidation. The basic concepts of impulse technology stem from Douglas Wahren's invention and vision of combining pressing and dewatering of paper by exposing the sheet to a heated pressing surface. Later, it was realised that high temperatures have the potential to modify and improve the paper surface. In its present form, the process is a direct evolution of the idea originally proposed by Wahren (1978) and later named "Impulse Drying" (Arenander and Wahren 1983). The wet pressing and drying operations can be combined into a single event by pressing the sheet in a nip formed between a felt-covered shoe and a solid roll. The latter is heated externally to temperatures exceeding 200 °C.

Impulse technology is aimed at decreasing the investment costs and reducing the operational costs of a paper machine (Stenström 1989; Persson 1994; Nilsson 1998). Although impulse pressing of paper uses high-grade energy for dewatering the sheet, it has generally been postulated to be economically advantageous for the following reasons:

- Uses less energy than conventional drying because all water may not need to be evaporated
- Permits substantially higher speeds and drying rates than conventional design
- Eliminates or strongly reduces capital costs for bulky drier sections, and associated peripheral equipment

This technology has the potential for energy saving and 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 levels 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.

As stated earlier, 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 properly balanced to produce a symmetrical sheet.

By increasing the dryness of the paper sheet from 50 to 51 %, there will be about 35 kg less water/t 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 must be taken into account. While for impulse drying high temperatures are required, steam cannot be utilised. 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, like electricity decreases the possible benefits for environment and the potential for profitability (Talja et al. 1998; SEPA Report 4712-4 1997a).

4.24.2 Energy Efficient Thermo-Mechanical Pulping (TMP) Processes

The 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 PGW (apart from some cases), which consumes less power (about 600–1200 kWh/ADt less) than TMP production for the same grades (SEPA-Report 4712-4 1997a; European Commission 2001). 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 KCL multistage process, which show 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 like RTS Thermopulp^{R}. RTS process combines conditions of a low residence time [R] at a temperature [T] exceeding the glass transition temperature of lignin and elevated disc speed [S]. These processes consume substantially less energy than “normal” TMP processes. Few examples for energy efficient development in TMP pulping are presented below:

4.24.2.1 High-Speed and High-Intensity TMP Refining

An example is the RTS refiner. It usually operates up to 2300 revolutions per minute and 5.5 bar over pressure. References are e.g. Norske Skog Walsum (DE), Norske Skog Golbey (FR), Holmen Halstavik (SE), Iggesund Paperboard, UK), UPM-Kymmene Stracel (FR), Norske Skog Follum (NO) (European Commission 2013). Several lines of the Thermopulp^{R} process went into operation both in Europe and North America in the mid-1990s. The first RTS installation was at Perlen Papier AG, Switzerland, in 1996. Both system 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 with acceptable pulp quality using this system.

4.24.2.2 Chip Pretreatment

Andritz has developed the RT Pressafiner pretreatment for chips to be treated before main-line refining (European Commission 2013). In the RT TMP process, the chips are first macerated in a pressurised RT Pressafiner chip press before entering the main-line refiners. RT treatment is being used at Holmen Braviken, SE, before single-stage DD refining, and in North America combined with RTS Twin SD-refiners. The reduction in specific energy consumption is about 10 %, i.e. 100–180 kWh/t. TMP mills that use this chip pretreatment may reduce their waste water load by using a washing stage (plug screw) before refining and bleaching. This reduces COD and the extractives content measured as DCM in the pulp by around 30 %. The low volume but highly concentrated pressate may undergo a specific waste water treatment (Gorski et al. 2009).

The objective of the RTS conditions, according to Andritz, is to thermally shock the wood fibre while in chip form, subjecting it to higher temperatures for a shorter period of time and thus making it more receptive to initial defibreization 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.

The concept of reduced energy consumption by increasing the disc speed of refining has been established using single disc and double disc 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. RTS is designed to avoid the shortcomings of the TMP process that produces stronger fibres but darkens the pulp. By exposing fibres to high temperatures while still in chip form, the heating occurs mainly through the lumina cavities, which means that the cellulose wall layers are heated first, while the middle lamella of the fibre has the least exposure to heat. The low-retention time at elevated temperature reduces thermal darkening reactions of the colour bodies associated with the middle lamella lignin. The result is a brighter and more easily bleached pulp. As for strength, most fractured fibres that are produced by a conventional TMP process occurs during primary refining. Since RTS softens chips by increasing fibre wall temperature prior to primary refining, fibre cutting is reduced, and fibre development is improved. Thus RTS can reduce or eliminate the requirement for kraft pulp in some paper grades. Also, RTS operation at high refiner disc speed reduces the residence time between refiner plates and increases specific refining power. This produces an improved pulp "fingerprint" that establishes potential pulp quality.

High-speed refining, is the key to improved operator efficiency. By subjecting thermally softened chips to higher refiner speeds for extremely short periods, high-speed refining can improve 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.

Energy savings must be balanced with investment cost. It can be expected that the new technology will only be implemented gradually due to the remaining lifetime of present equipment and plants (Lönnberg 2009).

4.24.3 New Energy Efficient Bleached Chemi-Thermo Mechanical Pulping Processes

For chemi-thermo mechanical pulping (CTMP) also, the main research work focused on energy reduction in refining. The production of conventional aspen chemi-thermo mechanical pulp at 250 ml CSF still requires 1350–1500 kWh/ADt.

Caustic application ahead of the primary refiner, decreases the applied specific refining energy and develops the strength properties. Different to the conventional CTMP, the P-RC APMP process (mild Preconditioning of the chips, Refiner Chemical Alkaline Peroxide Mechanical Pulping) uses alkaline peroxide solutions ahead of refining, which allows higher alkali charges before refining resulting in a decrease of refining energy down to 1050–1200 kWh/ADt at the same freeness. In addition, the efficient chip pretreatment yields well impregnated flexible fibres which can be refined to the required freeness level with low consistency refiners in the second stage and in reject, which drops the specific energy consumption by another 100–150 kWh/ADt without compromising strength properties. Most of the recent hardwood bleached CTMP installations apply the P-RC-APMP technology, which show the energy savings potential. Also low consistency refining in the second stage and in reject has been implemented in industrial operation with the desired results (Hill et al. 2009; Sabourin 2007; Sabourin et al. 2003).

4.24.4 Use of Enzymes During the Refining of TMP

The addition of enzymes to the wood chips between the first and secondary refiner can hydrolyze the hemicellulose and improve the fibre freeness of the cellulose fibres. This would allow to reduce the necessary time in the secondary refiner. The treatment with Novozym 476 (Cellulase) shows a significant saving of electricity in the second stage of refining and in the reject refiner by softening cellulose fibres (−160 kWh/t pulp). Kazymov (2010) studied the effects of pectinase, endoglucanase and a mixture of enzymes on three different size raw materials – normal size chip, crushed chip and water impregnated, instantly preheated, pressed and then fibreized at 400 kWh/t chip further named fibreized pulp showed that 5 kg/t of endoglucanase reduced the energy consumption by 20 % while the use of 1.5 kg/t of the mixture of enzymes produced a reduction of about 15 % of energy consumption during refining. Pectinase at different dosages to a maximum of 5 kg/t and different treatment times did not show significant effect on energy consumption. These results differ from those obtained by Sabourin and Hart (2010) who applied two pectinase treatments to TMP of black spruce (Picea mariana) wood chips and allowed to react for a period of 2.5 h. The average temperature during the reaction period was 47–48 °C. Enzymatic effects were studied on two refined pulps (1800 PFI revolutions). Pectinex 3XL® is a polygalacturonase, the enzyme protein used was separated and purified from Aspergillus aculeatus and Aspergillus niger. The application dosage was 720 g/t wood. The Novozyme 863® was a more aggressive enzyme preparation produced by a selected strain of Aspergillus aculeatus. This enzyme preparation contains polygalacturonase, other pectolytic activities, and a range of hemicellulolytic activities. It has the ability to disintegrate wood fibre cell wall material and works well in the temperature range of 25–50 °C. The application dosage was 830 g/t wood. The specific energy consumption was reduced by 9 % and 9.6 % respectively. The Pectinex 3XL® enzyme treatment successfully improved the tensile and tears indexes of the resulting pulp through specific surface activity in a desirable way while Novozyme 863® was somewhat harmful toward some of the desired pulp properties (Sabourin and Hart 2010). So far, this technique has been tested in several laboratory tests and on pilot plant scale. Also, short-term tests (1.2 weeks) have been carried out in the TMP line of UPMK Kymmene/Rauma mill. Main environmental benefit derived from the application of the technique would be the reduction of electricity consumption in the second refiner, due to shorter refining time. Trials made so far point out that energy savings in the reject refiners of up to 10–15 % could be possible.

4.24.5 Condebelt Process

The Condebelt drying process is a new paper drying technology that is based on the condensing belt principle. Metso developed the CondeBeltTM drying system in the early 1990s. It is being used in several mills in Europe and Korea. The system was originally designed as an alternative to a Yankee Dryer for high speed coated board machines. The process conditions experienced by the web during Condebelt drying are essentially similar to those prevailing in the so–called press drying experiments. Condebelt drying has been studied over a span of many years by means of several static units, as well as a pilot stage dynamic device. Based on these experiences, as well as several theoretical studies, designs have been developed for doing Condebelt drying as a production process. Condebelt drying is versatile, in that the process conditions can be changed to produce optimum quality for most paper and board grades. In this capability the Condebelt process is much superior to conventional cylinder drying.

In Condebelt drying, the paper is dried in a drying chamber by contact with a continuous hot steel band which is heated either by steam or hot gas. The water from the band is evaporated due to the heat from the band. This drying technology has the potential to replace the drying section of paper machine entirely, with drying rate 5 to 15 times higher than the conventional steam drying. However, condebelt drying is not suited for high basis weight papers. Although the technology is in use in Europe and Korea, it has found limited application in the United States.

The Condebelt process offers several advantages over conventional cylinder drying. 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 (max. 10 bar) and temperature (max. 180 °C) (Fig. 4.13). Heat is transferred from the hot band to the sheet, 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

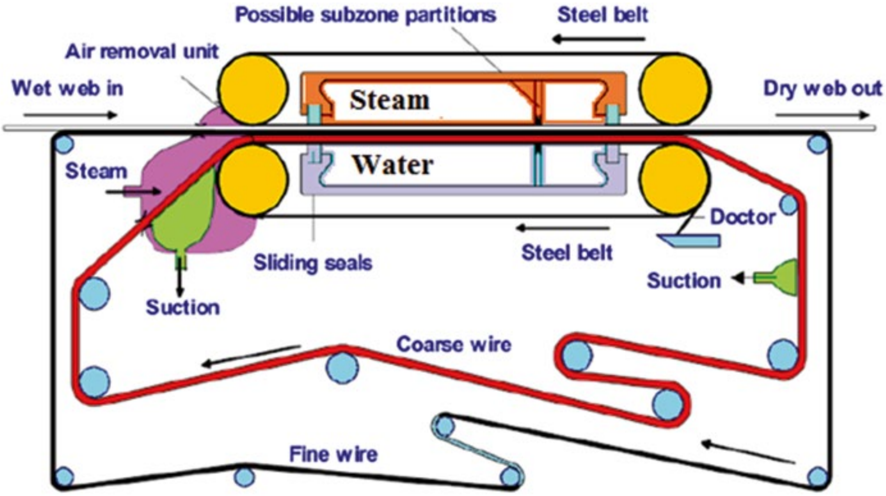


Fig. 4.13 Schematic of Condebelt drying process (Based on Lee et al. 2000)

machines is approximately 20 years and investment costs are extremely high (Retulainen et al. 1998; Ojala 1999). This drying process offers opportunities for

- Reducing the grammage of board
- Reducing the weight of corrugated boxes,
- Increasing the use of recycled furnishes and high-yield pulps

It is best suited to board grades, but also can be used for paper grades. In this process drying shrinkage of the web is eliminated, and even stiff fibres can effectively be plasticized and bonded to each other. Compared to cylinder drying, this results in improved strength properties, particularly in the cross-machine direction. Condebelt drying improves strength properties (20–60 %), surface smoothness, dimensional stability and resistance against humidity. In Condebelt drying, with recycled fibres it is possible to obtain the same strength values as with virgin fibres in conventional drying.

The disintegration of condensing belt dried board requires slightly more energy than cylinder-dried board. However, the recyclability of the board is good, especially when the re-made web is dried using the condensing belt process. The worsening of board properties after multiple recycling and condensing belt drying is quite moderate. This shows that condensing belt drying can form part of a ecologically sustainable paper cycle.

Presently, there are few Condebelt drying processes in commercial operation. Few mills have installed this technology (Retulainen 2001). One installation is 2.5 m wide with a machine speed of 200 m/min and has been running since 1996 at Stora Enso's Pankakoski board mill in Finland (Retulainen and Hamalainen 2000; Retulainen 2001). The other one is 4.5 m wide with a machine speed of 650 m/min and began operation in 1999 at Dong Il Paper Mfg. in South Korea, producing linerboard and fluting (Lee et al. 2000; Retulainen 2001). This technology can save an estimated 15 % in steam consumption (1.6 GJ/tonne paper) and can slightly reduce electricity consumption (20 kWh/tonne paper), with investment costs of $28/t paper for a retrofit and $110/t for new construction (Martin et al. 2000a). O&M costs are not expected to be significantly different from current practice (Xu et al. 2010). As a promising drying technology, Condebelt drying could be widely applied in the paper industry.

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 fibres can be manufactured without sacrificing product quality. Moreover, because of the improved paper sheet properties with Condebelt drying, it seems to be possible to use lower grade fibre 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 be used in other parts of the process also using heat pumping. The environmental benefits are potential savings of raw material (fibres, sizing agents) and a somewhat higher potential for energy recovery (Retulainen, 1998; Ojala 1999). Reductions in steam consumption are estimated to be 15 %, or 1.6 GJ/t-paper, with a slight reduction (~20 kWh/t-paper) in electricity consumption (Martin et al. 2000a). Capital costs are high. Investment cost of $28/ton paper has been estimated for retrofit installations, and $110/t for greenfield plants (1998 dollars) (Martin et al. 2000a).

4.24.6 High Consistency Forming

In the state-of-the-art papermaking process, paper products are formed from a low consistency water suspension approximately 0.6–1.0 % made up of fibres, fillers and chemicals. This suspension is pumped through a head-box that spreads it on a plastic wire. With the complex design of the head-box, sufficient turbulent flow conditions are created to control the homogeneity of the papermaking suspension through the subsequent drainage process. Due to low consistency, chemicals have to be used to increase the retention of furnish components on paper. The recovery of un-retained material and water consumes a lot of energy and requires numerous unit operations and pieces of process equipment. Thus increasing consistency would be a technological step forward for papermaking.

High consistency (HC) forming was first introduced in the late 1960s when the industry was concerned about the cost of wastewater treatment. In high consistency forming, the furnish which enters at the forming stage has more than double the consistency (3 %) than normal furnish. This measure increases forming speed, and reduces dewatering and vacuum power requirements (Maleshenko et al. 2008; Gullichsen et al. 2009; Elaahi and Lowitt 1988). Application of this technology is limited to specific paper grades, especially low-basis weight grades such as tissue, toweling, and newsprint. Electricity savings are estimated at 8 % that is about 41 kWh/t of paper (Elaahi and Lowitt 1988; de Beer 1998). High consistency formers are expected to cost $70/t of paper with an additional maintenance cost of $0.72/t (Jaccard and Willis Enterprises Associates 1996), also assuming that new paper machine wet ends are similarly costly. This measure is applied to 20 % of current paper production with exclusion to light grade. HC forming will give a strong advantage to the pulp and paper industry as such a system can reduce not only energy but also the use of chemical additives. HC forming integrates well with closed water circulations and with new heat recovery techniques, and surface treatment methods. Furthermore, new types of products can be manufactured. HC papermaking will reduce pumping costs, increase the retention of fibres with fewer chemicals, and simplify the wet end process. Together with closed water circulation and higher process temperature, high-consistency forming may lead to a dramatically reduced energy consumption of the production line. The HC system creates a new platform for the production of many different paper and board products which will form a paradigm shift in paper production.

It is expected that HC short circulation process will consume 50 % less energy and 30 % less vacuum energy, and that the capital intensity of the process will be reduced by 30 %. Due to improved retention, the consumption of chemicals and the environmental load of the process will also be reduced. Increasing the consistency in forming was initially studied already in the 1980s, e.g. in Finland but with little success. The early studies resulted in unacceptable sheet quality due to the difficulties in maintaining sufficient turbulence during web drainage. However, during recent years, substantial progress has been obtained through the integration of head-box and drainage. The operation window of current machines can most likely be widened by optimising the whole process, e.g. raw-materials, machinery, clothing and chemicals. This can however lead to difficulties in dewatering or runnability of the paper machine. The control of fluidisation and the screening of high-consistency stock together with product quality, have been found to be major difficulties to overcome. A breakthrough in HC papermaking would require new technology where current unit operations, i.e. head-box, drainage and pressing are integrated together in a compact way, resulting in desired paper structures from high-consistency furnish. The HC papermaking process would require that the approach and short circulation systems, fluidisation and dewatering processes take place at high consistency. Progress is needed in the mixing of fibres and chemicals and in screening, air removal, fluidisation, dewatering of furnish, and in process control. The development of reliable measurement system for the process including web properties is one of the key tasks for process control. Modeling is needed in dimensioning the process and in analysing and determining the optimal process concept. Stability of the process is one of the major concerns. With regard to raw material control, soft sensors and new measurement techniques will make it possible to identify incoming material properties, and thus make it possible to take the optimisation and control further in a proper way. Overall dynamic energy system analysis using simulation and optimisation will provide solutions that reduce energy losses compared to what is obtainable with state-of-the-art steady state analysis, e.g. the pinch method. By orchestrating the production entities dynamically, the intermediate buffers can be radically reduced. This leads to major energy savings in production systems due to, e.g. less pumping, and both energy and capital savings in new and rebuilt production systems.

Fresh water is introduced to the HC process as shower water and as dilution water of the chemicals just like in modern processes. To reduce the use of fresh water, the output streams from screening and fibre recovery should be low in volume and the combination of former and fibre recovery units should result in high quality circulation water that has a very low concentration of solids and dissolved and colloidal substances.

High-consistency forming of paper products requires new innovative process solutions that will significantly reduce the energy and water consumption in papermaking processes. Pilot scale studies aimed towards HC papermaking are under way. Modelling and simulation tools will be an integral part of the development work both at the unit process level and in analysing how mill concepts will be changed as a result of HC forming. New measurement techniques will be used in the development of models and control methods of the forming process.

4.24.7 Black Liquor and Hog Fuel Gasification

Black liquor gasification (BLG) is an emerging technology with a long research and development history. BLG entails pyrolyzing concentrated black liquor into an inorganic phase and a gas phase through reactions with oxygen or air at high temperatures. BLG technology can be an alternative to using a recovery boiler to produce electricity, chemicals, or fuels such as dimethyl ether (DME), synthetic gas (syngas), methanol, hydrogen, or synthetic diesel (Naqvi et al. 2010, 2012). BLG can also be integrated with combined-cycle (CC) technology (BLGCC), which has potential to produce significantly more electricity than current boiler/steam turbine systems and could even make the mill an electricity exporter (Martin et al. 2000b). Alternatively, the syngas can be used as a feedstock to produce chemicals, thereby using the pulp mill as a biorefinery (Worrell et al. 2004, 2010).

There have been several demonstration and commercial units built for both black liquor and hog fuel gasification. All existing units in the United States have been atmospheric units. Gasification is a promising technique for pulp mills for the generation of surplus of electrical energy but yet to achieve widespread acceptance. Production of a combustible gas from various fuels – coal, wood residues, black liquor – is possible through different gasification technologies. The principle of the gasification of black liquor is to pyrolyse concentrated black liquor into an inorganic phase and a gas phase through reactions with oxygen (air) at high temperatures.

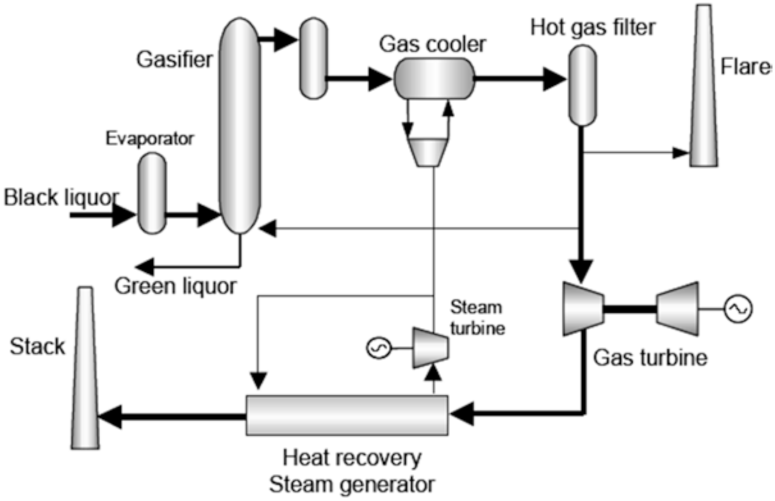


Fig. 4.14 Integrated gasification and combined cycle (IGCC) (Based on Sricharoenchaikul 2001)

Gasification may become part of integrated gasification and combined cycle (IGCC) operation, or lead to pulp mills becoming biorefineries (Larsen et al. 2003). Figure 4.14 shows a 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, and the condensed phase is left behind. The syngas is cleaned in order to remove particulates and tars and to absorb inorganic species which are alkali vapour species, sulphur dioxide, and hydrogen sulphide. This is performed to prevent damage to the gas turbine and to reduce emissions of the pollutants. The clean syngas is burned in gas turbines coupled with generators to produce electricity. Gas turbines are inherently more efficient than the steam turbines of recovery boilers because of their high overall air fuel ratios (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 continuously leaves the bottom of the gasifier and must be processed further in the lime cycle for recovering pulping chemicals.

In recovery boilers, virtually all of the alkali and sulphur species leave in the smelt mostly as sodium sulphide and sodium carbonate, but in gasifiers, there is a natural partitioning of sulphur to the gas phase (mainly hydrogen sulphide) and alkali species to the condensed phase after the black liquor is gasified. Because of this inherent separation, it is possible to use alternative pulping chemistries that would result in higher amounts of pulp per unit of wood consumed (Larsen et al. 1998, 2003). Gasification at low temperatures thermodynamically favours a higher sodium/sulphur split than gasification at high temperatures. This actually results in higher amounts of sulphur gases at low temperatures. A large amount of the black liquor sulphur species leaves the low-temperature process as hydrogen sulphide. It may be recovered via absorption to facilitate alternative pulping chemistries.

Compared to the current technology, the partitioning of sodium and sulphur in black liquor gasification requires a higher capacity for the lime cycle. The sodium/sulphur split results in a higher amount of sodium carbonate in the green liquor. This is because less sulphur is available in the smelt to form sodium sulphide. For each mole of sulphur that goes into the gas phase, one more mole of sodium carbonate is produced in the condensed phase (Larsen et al. 2003). The increase in sodium carbonate results in higher causticization loads, increases in lime kiln capacity, and increases in fossil fuel consumption to run the lime kiln. 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 can be conducted at low temperatures and also 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 sulphur 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 clean-up operations in addition to contaminating gas turbines upstream of the gasifier. These contamination problems may result in a loss of fuel product from the gasifier (Sricharoenchaikul 2001). Low temperature gasification processes work below 715 °C and the inorganic salts are removed as dry solids. High temperature processes operate above 900 °C and an inorganic salt smelt is obtained.

Several companies conducted trials to develop a commercially feasible process for black liquor gasification (Whitty and Baxter 2001; Whitty and Verrill 2004). However, currently only two technologies are being commercially pursued:

MTCI (low temperature) (Durai-Swamy et al. 1991; Mansour et al. 1992, 1993, 1997; Rockvam 2001; Whitty and Verrill 2004)

MTCI has two projects running today, both in mills with a sodium carbonate 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 ton dry solids per day and is fully integrated with the mill (DeCarrera 2006). The second project is for the Norampac Trenton mill, Ontario, Canada which had no chemical recovery before the steam reformer commission began 2003 (Middleton 2006; Newport et al. 2004; Vakkilainen et al. 2008). This gasifier has a processing rate of 115 ton DS/day.

Chemrec (high temperature) (Brown and Landälv 2001; Kignell 1989; Stigsson 1998; Whitty and Nilsson 2001; Whitty and Verrill 2004).

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. Chemrec has built and operated a black liquor gasification plant in Piteå in northern Sweden and later together with partners added a bio-DME synthesis plant on the same site. The subsidiary owning this development plant is now sold to Luleå University of Technology for the plant to be used in continued R&D work. The pressurized, oxygen-blown gasifier of this plant has till date been operated more than 18 000 h, consistently producing syngas of very good quality. The system includes the processes of gasification and quenching, gas cooling and gas cleaning. The produced gas has been determined to contain the following gases (Lindblom 2006):

- 41 % hydrogen
- 31 % carbon dioxide
- 25 % carbon monooxide
- 2 % methane
- 1.4 % hydrogen sulphide

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 4.15 shows the CHEMREC DP-1 plant.

Since 2011 the syngas produced has been used for synthesis of bio-methanol and bio-DME (dimethyl ether). The bio-DME produced has been used in very successful heavy truck fleet trials conducted by Volvo Trucks within the pan-European BioDME project. Overall, this extended period of operation has validated the Chemrec gasification concept and provided all information required for commercial-scale implementation. Effective from Dec 31, 2012 these plants have been transferred

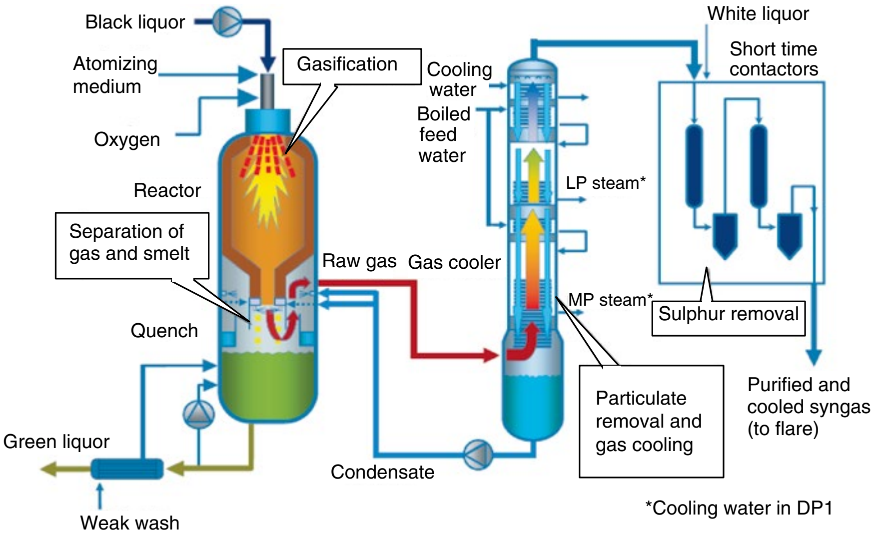


Fig. 4.15 The CHEMREC DP-1 plant (Source: www.chemrec.se/admin/UploadFile.aspx?path=/UserUploadFiles/2005%20DP-1%20brochure.pdf. Reproduced with permission)

to Luleå University of Technology (LTU). Also the operating and development personnel at the plant are now employed by LTU. In December 2012, the Swedish Energy Agency approved funding supporting the continued operation of the plants to make it available for new research and development programs. Chemrec actively participates in these programs and has retained the right of access to the plant for future trials, e.g. with feedstock of specific customers. Chemrec in its new form will thus for further development work rely largely on this new network structure and the core organization will be heavily focused on the commercialization of the technology.

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 (Di Methyl Ether). The new combined pulp and chemicals 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-scaled 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 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 sulphur 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 make-up 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 tds/d) commercial atmospheric units have been built (Bajpai 2010; Naqvi et al. 2010). 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.

The following benefits and costs have been identified for BLG (Worrell et al. 2004; Gebart 2006; IEA 2009; Cheremisinoff and Rosenfeld 2010; Program 2011; Chemrec 2012):

- Increases pulping process energy recovery by 10 %
- Increases power production by two to three times at the pulp mills that exported electricity sold to power grid
- BLGCC system has investment 60–90 % higher than for standard boiler system, ranging from $200–400 million
- Increases pulp yield by about 5–7% if done in conjunction with significant changes in pulping conditions

Even though there are significant gains to be made, there still remain many unresolved issues (Tucker 2002 and Katofsky et al. 2003) listed below:

- Finding materials that survive in a gasifier
- Mitigating increased causticizing load
- How to startup and shutdown
- Tar destruction
- Alkali removal
- 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 2–3 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/a. 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.

4.24.8 Partial Borate Autocaustising

This technique makes it possible to produce caustic (sodium hydroxide) directly in the recovery boiler and improves the lime kiln and recausticisation operations by reducing causticising loads and the amount of lime processed through the system. The partial borate autocausticising process occurs when sodium borates are added to the kraft liquor at sub-stoichiometric levels (Björk et al. 2005). A portion of the sodium carbonate is causticised in the recovery boiler. The causticisation of the remaining sodium carbonate is completed in a conventional recausticising plant of the pulp mill with a reduced quantity of lime. The technology may appear as an attractive option particularly for kraft pulp mills where incremental causticising and lime kiln capacity are required. Mill-scale trials have shown that there are no major side effects on the mill operations. The major findings of the studies suggest that borate present in cooking liquor presents the following advantages (Bujanovic et al. 2003; Eckert et al. 2005):

- Increases pulp yield
- May decrease rejects
- Improves the selectivity of lignin removal
- Can increase pulp viscosity at the same kappa number
- Does not require capital investment since the autocausticising reaction occurs in the existing recovery boiler

The principal autocausticising reaction that takes place in the recovery boiler furnace occurs between sodium metaborate and sodium carbonate in the molten smelt to form trisodium borate. The critical parameters of the process are the temperature and Na/B ratio in the black liquor. Trisodium borate reacts with water in the smelt dissolving tank to form sodium hydroxide and regenerate $NaBO_2$ (Tran et al. 2001; Bujanovic et al. 2003; Michniewicz and Janiqa 2010). The partial borate autocausticising process occurs when sodium borates are added to the kraft liquor at sub-stoichiometric levels (Björk et al. 2005). A portion of the sodium carbonate is causticised in the recovery boiler. The causticisation of the remaining sodium carbonate is completed in a conventional recausticising plant of the pulp mill with a reduced quantity of lime. The technology may appear as an attractive option particularly for kraft pulp mills where incremental causticising and lime kiln capacity are required. Mill trials have shown that there are no major side effects on the mill operations. The success of the technology depends greatly on whether the boron-containing black liquor can be effectively processed in a recovery boiler, and on the degree of completion of the reactions that produce trisodium borate in the boiler. Promising environmental benefits are connected with a reduction of the emissions from the lime kiln and a reduced consumption of energy or fuel by a lime kiln.

Several mill trials with partial borate autocausticisation have been conducted and the problems encountered have been resolved. The technology is now being used at several mills in Sweden, Brazil, Indonesia and the United States. The results show that the technology works. It allows the lime consumption to be reduced by an amount proportional to the level of autocausticisation (depending on the Na/B molar ratio in the liquor cycle). No negative effect has been found on pulp properties, equipment corrosion, digester operations, pulp washing, black liquor evaporation, recausticizing and lime kiln operations. For a greenfield kraft pulp mill, with proper equipment design and operation, the technology has the potential to eliminate completely the causticisation plant and lime kiln, making the kraft process much simpler (Hoddenbagh et al. 2001; Kochesfahani and Bair 2002; Kochesfahani et al. 2006).

Six mill trials are reported by Kochesfahani and Bair (2002), who carried out short-term trials to evaluate the effect of the technology on specific parts of the mill, and long-term trials to demonstrate the overall effects of the technology on the mill operations. At autocausticisation levels up to 25 %, no undesired effects could be observed on digesters, pulp quality, brownstock washing, black liquor evaporation, lime recausticisation or kiln operations. The most apparent effect of autocausticisation on the liquor cycle is the increase in total inorganic salts in the system. This leads to an increase in the throughput of solids for evaporators, concentrators and recovery boilers. Because of the endothermic nature of the autocausticisation reaction, the black liquor heating value decreases. The evaporation load is not affected, however, and so the temperature may decrease in the recovery boiler. Even though Kochesfahani and Bair (2002) report the conversion of autocausticisation to be sensitive to operation conditions, especially temperature, they claim that the overall impacts on the recovery boiler are manageable.

Partial borate autocausticizing may offer cost savings and environmental benefits to kraft pulp mills that are recausticising-limited by relieving production bottlenecks in the liquor cycle without costs for the capacity growth of the conventional causticisation plant and lime kiln. The benefits are obtained through decreasing the lime kiln load and fuel usage or reducing fresh lime purchases and lime mud disposal. Some benefits also result from the increase in pulp yield at the digester and/or potential decrease in alkali charge. However, addition of borate increases the solids content in fired black liquor, especially at high levels of autocausticising and may result in a decrease in black liquor heating value and in steam production (Mao et al. 2006; Tran et al. 2001; Bujanovic et al. 2003; Michniewicz and Janiqa 2010; Björk et al. 2005;Eckert et al. 2005).

4.24.9 Biorefinery

Much has been discussed about biorefinery concept in recent years (Bajpai 2012a). It was a subject mentioned in President Bush's 2006 State of the Union Address. It is a component of AF&PA's Agenda 2020. Extracting hydrogen, and other chemical feed stock, from wood chips prior to pulping has the potential for a significant change in the way pulp mills utilize/produce energy. Net energy efficiency impact of a biorefinery is currently being investigated . The development of an integrated forest biorefinery (IFBR) would enable the industry to increase its revenue by producing bioenergy and new biomaterials in addition to traditional wood, pulp and paper products. The IFBR concept also addresses the societal need to use renewable resources rather than fossil fuels to produce commodity products, liquid fuels and electricity. The initial visualised IFBR would be based on sulphur-free, alkaline pulping of hardwood with an alkaline hemicellulose extraction step prior to pulping and spent pulping liquor gasification and lignin precipitation after pulping. New products from an IFBR based on alkaline pulping include electric power, new wood composites, liquid fuel, ethanol, chemicals and polymers. Pre-extraction generates a feed stream for new bioproducts, while decreasing alkali consumption, increasing delignification rate and reducing black liquor load (Jönsson et al. 2011; Mäkinen et al. 2011; Wang et al. 2012; CEPI 2009). Black liquor gasification and/or lignin precipitation are an integral part of the IFBR, with the synthesis gas and precipitated lignin being the feed for liquid fuel and carbon fibres, respectively. The additional energy requirements of the IFBR would be met by gasification/combustion of waste biomass. The key to the successful implementation of the forest biorefinery is to identify possible products that can be economically produced by a pulp and paper mill. Process integration tools can be used to identify these products. A roadmap can be developed once the products have been identified. The successful implementation of the forest biorefinery will likely be mill specific, and will in many cases require strategic collaborations with experts.

4.25 Partial System Closure

The pulp and paper industry is faced with mounting environmental, political and economic pressures to reduce the volume and toxicity of its industrial waste water. During the last few years, the concept of system closure has been gaining popularity in the forest products industry. Bleach plant closure, through filtrate recycle, to the recovery cycle, is becoming attractive in light of the stringent environmental regulations (Johnson et al. 1996; Gleadow and Hastings 1995; Gleadow et al. 1996; Albert 1995, 1997; Bajpai and Bajpai 1999). Complete closure, however, is difficult with chlorine-based sequences, because the resulting bleach liquor chloride level is a threat to the recovery boiler. No bleach plants at papergrade bleached kraft mills are known to be operating effluent-free on a continuous basis. 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. Fibreline 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.

Partial closure of the bleach plant and other mill systems, leads to increased concentrations of organics (dissolved wood compounds) and inorganics, often called non-process elements (NPE). Consequences of this are listed below:

- Increased corrosion in digesters, evaporators and recovery boilers
- Depression of recovery boiler capacity and efficiency
- Scaling and deposits in bleach plants, digesters and evaporators
- Increased consumption of chemicals
- Variable pulp quality.
- Efficiency of a Q stage in removing transition metal ions is reduced by extensive system closure due to the inhibition created by the Donnan effect (KAM Report A100 2003).

Therefore, before implementing a closure strategy, the consequences for mill operations listed below have to be analysed:

- Mill uptime
- Construction materials

- Mill personnel safety
- Pulp quality

Kraft mill bleach plant effluent flows usually range from 10 to 30 m^3/ADt in modern mills. Many European mills have flows between 15 and 25 m^3/ADt. Few mills have bleach plant effluent flows under 10 m^3/ADt. There are still many mills having bleach plant effluent flows above 30 m^3/ADt. The two main strategies for bleach plant closure are presented below (Beca AMEC 2004):

Increased recycle of filtrates within the bleach plant –

This results in reduced fresh water consumption and bleach plant effluent flows. However, it does not lead to a reduction of specific emissions like AOX and COD on a mass basis (example kg/ADt)

Recycle of bleach plant filtrates to the recovery system –

Only alkaline bleach plant filtrate is recycled generally, but a few mills also recycle acidic filtrate. The filtrate can be used as partial replacement of wash liquid in the fibreline brown stock washing, or directly recycled to the recovery area. Any of these two methods reduces the emissions in terms of AOX, COD and other environmental parameters on a mass basis (example kg/ADt). The fresh water consumption and effluent flow may also decrease, but not necessarily.

Currently, ECF effluents cannot be easily recycled to chemical recovery due to the build-up of chloride ions and in some cases potassium, and scaling/deposition of organic and inorganic compounds. The COD loads of BEKP mill bleach plant effluents are about 20–30 kg/ADt for ECF bleaching and 20–35 kg/ADt for TCF bleaching at a kappa number of 8–12 to the bleach plant and with no recovery of bleach plant filtrates. Partial recovery of bleach plant filtrates has the potential to reduce COD emissions by up to 30 %. The adverse effects of partial bleach plant closure are presented below:

- Partial closure of the bleach plant and other mill systems leads to increased concentrations of organic and inorganic compounds, also including NPE, resulting in increased corrosion, scaling and deposition within the bleach plant and other mill areas
- The accumulation of dissolved solids causes a considerable increase in the consumption of bleaching chemicals
- Difficulty in reaching target brightness
- Variable pulp quality
- pH adjustments with sulphuric acid and sodium hydroxide may be costly because of the considerable buffer capacity of the pulp. The sodium-sulphur balance of the mill may, therefore, be disrupted.
- Large buffer storage capacity for filtrates is necessary to absorb transient and upset conditions, whose frequency increases with the degree of closure.
- Precipitation of calcium oxalate, calcium carbonate and barium sulphate. Precipitates of calcium oxalate are dominant at pH values lower than 8 while calcium carbonate precipitates at pH 8–12. Barium sulphate precipitates over the entire technically interesting pH range (2–12) (KAM Report A100 2003)

Table 4.37 Kraft mills (paper grade) practising bleach plant filtrate recovery

Mills	Bleaching agents/sequence	Filtrates recovered
Södra Cell – Mörrum, Sweden	O, P, Q, D	Alkaline
Södra Cell – Värö, Sweden	O, P, Q	Alkaline
M-Real Sverige AB Husum, Sweden	O, D, E, P	Acid, alkaline
	O, Z, E, P, D	All – part time
Aspa Bruk – Munksjo, Sweden	OQ(PO)	Q, PO
	OQ(PO)DD	O, PO
SCA – Östrand, Sweden	OOQ(OP)(ZQ)(PO)	Alkaline
Stora Enso – Skoghall, Sweden	O(PO)DQ(PO)	PO
Metsä-Botnia – Rauma, Finland	O(ZQ)(PO)(ZQ)(PO/PO)	PO
UPM-Kymmene Wisaforest- Pietarsaari, Finland	O(ZD)(O/EO)(ZD)EP	Z/D, OP
	O(ZQ)(OP)ZP	Z/D, EOP, D, P
	OW(Z/D)(EOP)DP	
Blue Ridge Paper – Canton, NC	OD(EOP)D	D, EOP
	OD(EO)D	EO
International Paper – Franklin,	OZED	Z, E
Samoa-Pacific – Samoa, CA	OQQPQ(PO)	P, PO

Based on Beca AMC (2004, 2006)

- A control strategy for water management in the plant has to be developed and implemented.
- Additional evaporation plant capacity and additional recovery boiler capacity may have to be installed

A number of mills are currently practicing of bleaching filtrate recovery. Table 4.37 shows the list of paper grade Kraft mills practicing recovery of bleach plant filtrate (Beca AMEC, 2004). In all cases the filtrates are recovered via the pulp washing line. Filtrates are recovered from both ECF and TCF bleach plants, and the challenges of closure are to a great degree the same for all bleach plants. Apart from the mills, shown in the table, there may be other mills practicing filtrate recovery (Stratton and Gleadow 2003). The original intent for many of these mills was to completely eliminate bleach plant effluents. Mills have generally found that as the degree of closure increases, incremental benefits decrease and technical challenges increase. Complete closure appears to be significantly more difficult to achieve than expected. Most mills have found that operations can be sustained only under partially closed conditions. Furthermore, several of the mills in Sweden have concluded that partial closure coupled with secondary treatment of the remaining effluent represents a more optimal solution than full closure. In order to reduce operating problems, several mills have decided to decrease the degree of bleach plant closure.

There are three essentially closed-cycle bleach plants in operation in Swedish mills that bleach a portion of their total pulp production in addition to the mills presented in Table 4.37. In these mills, a small bleach plant was added to an existing brown paper and board mill in order to produce white top liner. Alkaline filtrates from bleaching are recycled countercurrently to brown stock washing. The neutral or acidic filtrate is returned for washing brown stock in two of the mills, and in the third mill it is concentrated in a low temperature evaporation stage; the concentrate is added to the black liquor concentrators. The bleached pulp production represents only 20 % of production in SCA Munksund and Kappa Kraftliner Piteå (formerly AssiDomän Lövholmen) mill and in AssiDomän Frövi, 40 % of production is bleached. The small capacity of these bleach plants relative to the total capacity of the brown stock system and chemical recovery facilities provides conducive conditions for recovering of bleaching filtrates compared with papergrade bleached kraft mills where all of the pulp is bleached.

There are no bleach plants at paper grade bleached kraft mills that operate fully closed on a continuous basis. A number of relatively 'closed' new bleaching lines using presses have been built or are under construction. Some perform with bleaching effluent flows from 6 to 9 m^3/ADt, including Advance Agro in Thailand, Stora Enso Skoghall and SCA Östrand in Sweden, and ZP Rosenthal in Germany. Several mills practice recovery of alkaline filtrates via the post-oxygen or brown stock washers. A few mills are recovering acidic bleaching filtrates, and few linerboard mills have small bleach plants for top liner production from which all of the filtrates are recycled to associated base liner brown stock systems (Beca AMC 2006; Ernerfeldt et al. 1999).

4.25.1 Control of NPE with Partial Closure

Process closure in general and particularly bleaching wastewater recovery, can lead to increased concentrations of so-called non-process elements (NPEs). NPEs can cause several problems as mentioned before if allowed to accumulate in mill process streams. The degree to which filtrate recovery can be practiced is limited by the availability of means to effectively manage these and other impacts (Stratton and Gleadow 2003). Important sources of NPEs are raw materials, especially wood, water, and makeup chemicals. NPEs can be classified according to the kinds and locations of impacts they have.

- Chlorine which exists almost exclusively as chloride ion in mill liquor streams and potassium have adverse impacts on recovery furnace operation
- Calcium and barium can form scale deposits in the bleach plant and at locations where acidic bleaching filtrates are recovered
- Manganese, iron, and copper consume certain bleaching chemicals and the subsequent degradation products can cause pulp strength losses
- Silicon and aluminum form scale deposits on heat transfer surfaces

Several technologies are available to manage the impacts of NPEs (Stratton et al. 2003). There are potentially significant impacts associated with certain transition metal ions, including Mn+2, Fe+3, and Cu+2, that catalyze the decomposition of peroxide. In ozone bleaching, Fe + 3 and Cu + 2 can result in significant degradation of cellulose. This can be attributed to free radical species produced by reactions involving these ions (Chirat and Lachenal 1994). In order to limit the impact of transition metals in ozone and peroxide stages, provisions are made to sequester and/or remove these ions. Chelating agents, especially EDTA, are used in a Q stage just before the peroxide stage. The chelating agent affect their removal from the pulp and chemically isolates them in a dissolved state; they are subsequently washed from the pulp and discharged with the Q stage filtrate. In ozone bleaching, the unbleached pulp is treated with acid at a pH of about 2 to remove the transition metals, followed by washing to remove the dissolved metals ions. The acid treatment also provides the optimum pH for ozone treatment (van Lierop et al. 1996). Transition metal ions do not appear to influence chlorine dioxide bleaching. In addition to the transition metals, kraft pulps contain alkaline earth metals, particularly calcium and barium. These metals originate in the wood and as lime mud particles in the white liquor. They remain chemically or physically bound to the pulp through the fibreline, dissolving in the first acidic stage of the bleach plant, typically the first D stage, Q stage, or Z stage. The acid filtrate discharge serves as a purge for metals in a conventional open bleach plant. As closure is practiced, a purge of these metals must be maintained, as they will precipitate onto the pulp if acidic filtrate is recycled to the alkaline brownstock or post-oxygen washing systems. The precipitated metals would then be carried forward into the bleach plant where they would be re-dissolved. Finally, the concentration in this loop would build until scale deposits formed, plugging washer drums and causing downtime to remove the offending material. This phenomenon has been referred to as an acid/base trap or, specifically, a metals trap. Closure of a bleach plant, whether ECF or TCF, cannot be achieved without new provisions for purging or stabilizing metals from acidic filtrates. Aluminum and silicon are two other elements that can cause problems in a kraft mill. These elements combine with each other and various anions to create scale deposits on heat transfer surfaces particularly in the black liquor evaporators. Although they are not removed as efficiently as other metals such as manganese and iron, aluminum and silicon are co-precipitated as double or triple salts and removed with the green liquor dregs. One method to purging metals from the acid bleaching filtrate is to install an auxiliary system to remove the metal ions from the acid filtrate. Chemical precipitation and ion exchange have been examined as metal removal schemes. By addition of sodium hydroxide and sodium carbonate, or by adding green liquor, precipitation of metal hydroxides and carbonates can be obtained (Lindberg et al. 1994). The BFR process developed by Champion International includes a treatment of acid filtrate such as chemical precipitation or ion exchange (Maples et al. 1994). Another method for purging metals is to operate an acid wash stage with a low volume purge. Sulphuric or other acid is added to control the pH below a value of 4, and the pulp is washed to limit metals carryover into the first bleaching stage. Some of the acid filtrate can be recycled to the fibreline, as long as a sufficient purge stream is maintained. This purge will contain some organic compounds. However, some of the organics, particularly high molecular weight lignin fragments, will tend to partition onto the pulp under acidic conditions

(Joseph and White 1996). This scheme is practiced on the OZED bleaching line at the bleached kraft mill in Franklin, Virginia. The oxygen delignified pulp is treated with acid and dewatered before the ozone (Z) stage. A purge is maintained to control metals, and the Z and E stage filtrates are recovered via the post-oxygen washers. Control of aluminium and silicon is difficult because they are relatively soluble in alkaline liquors compared to other metals. Reducing inputs by utilizing makeup lime with low levels of these elements may be an effective approach. They are more soluble in white liquor than in green, so efficient dregs removal can reduce buildup of these elements. Addition of magnesium salts to green liquor can remove aluminum and silicon by precipitation of minerals and subsequent removal with the dregs (Wannenmacher et al. 1998).

Phosphorus is introduced into the mill primarily with the wood supply (Ulmgren and Rådeström 1997). The primary purges for phosphorus include the bleaching filtrates or unbleached pulp, grits, dregs, and lime mud losses. Recovery of bleaching filtrates can reduce or eliminate an important purge point for phosphorus. Its primary impact is that it can accumulate in the lime cycle as calcium phosphate thereby reducing the chemical availability of the lime and increasing lime requirements. Increased purging of lime mud has been suggested as a corrective action, although the increased fresh lime makeup could bring additional aluminum and silica into the liquor cycle (Ulmgren and Rådeström 1997). Dissolved organic matter consumes bleaching chemicals.

Closure of the bleaching process increases the concentrations of dissolved organics. Therefore, increase in the usage of bleaching chemicals usage is expected. The source of the organic compounds is a key variable in determining the amount of bleaching chemicals consumed (Stratton et al. 2003). The organics from cooking (black liquor) consume more chlorine or chlorine dioxide than solids generated in oxygen delignification. This in turn consume more chemicals than bleach plant extraction stage organics (Canovas and Maples 1995). Generally, organics produced in chlorine dioxide stages are well oxidized and consume only minor amounts of chlorine dioxide. The primary means of mitigating the effect of organic matter on bleach chemical use is efficient washing, particularly after oxygen delignification. In this regard, the performance of pulp washing equipment is the most important consideration. Organic compounds in the wood termed as extractives, can result in pitch deposits on process equipment and in the product. Pitch is of special concern in acid or neutral sulfite mills, as the resinous material is not saponified as in case of most alkaline pulping systems. Traditional methods of controlling pitch are through the use of dispersants, fixation agents and talc. Process closure at mills is likely to increase pitch accumulations. Kemira Chemicals Oy has developed a process to remove extractives from process filtrates. This process utilizes polyethylene oxide flocculant and flotation separation. The process was first implemented at the Domsjö Fabriker sulfite mill in Sweden. This enabled closure of its TCF bleach plant. The process appears to be also effective on kraft mill filtrates. The resulting pitch-containing residue may be suitable for burning in a wood waste fired boiler (Rampotas et al. 1996).

The elemental chlorine enters a kraft mill as the chloride ion with the wood and the makeup chemicals such as sodium hydroxide. Chloride is extremely soluble in the alkaline liquors of the kraft cycle, and accumulates there. The typical chloride purge points in a mill are:

- Recovery boiler stack emissions
- Washing losses from brownstock or post-oxygen washing into the bleach plant
- Losses of green, white and black liquor

Because process closure reduces such losses, chloride and potassium concentrations will increase unless alternative purge means are provided. There are several ways to manage Cl and K impacts. Coastal mills in British Columbia, Canada, are designed to cope with very high Cl levels due to seaborne wood. In particular, the recovery boilers at these mills are designed with larger superheater sections so that the upper furnace temperatures are somewhat lower than in units of more common, inland designs. The lower temperatures reduce the potential for the condensed fume particles to accumulate in areas where the flue gas passages are narrow and easily plugged.

A few techniques are being used by mills to control Cl and K levels in their liquor systems. These techniques generally have limited effectiveness, and so are not generally sufficient where recovery of ECF bleaching filtrates is practiced. A relatively simple measure is to use only makeup chemicals, especially caustic, with very low Cl content. Another commonly used technique is to periodically purge some of the recovery boiler precipitator catch (the condensed fume from the furnace), which is enriched with Cl and K compounds. Normally, this chemical ash collected by the electrostatic precipitator is returned to the black liquor just before firing. The purged ash may be dissolved in water and discharged as a low volume brine wastewater. This technique is generally ineffective because the ash, while enriched in Cl and K, consists mostly of sodium sulphate, and any loss of sodium and sulphur represents a loss of pulping chemicals. Higher Cl and K purge amounts can be obtained by separating the Cl and K from the ESP catch so that most of the sodium and sulphur is returned to the liquor cycle. The simplest process to achieve this is to leach the Cl and K from the ESP catch, taking benefit of the higher solubility of NaCl and KCl compared to Na_2SO_4. The liquid phase is then sewered and the saltcake (Na_2SO_4) is returned to the black liquor. This method is being used at International Paper's Mogi Guaçu mill in Brazil. Higher Cl and K removals and saltcake recovery efficiencies can be achieved by completely dissolving the ESP catch and crystallising the Na_2SO_4 by evaporation or cooling. The crystals are separated by filtration or centrifugation and returned to the black liquor. Two basic versions of this process have been developed. One version generates Na_2SO_4 decahydrate, Glauber's salt, and the other generates anhydrous Na_2SO_4. The first version, developed by Mitsubishi, involves acidifying the dissolved material to remove carbonates by purging carbon dioxide, and concentrating the solution by evaporative crystallisation. Glauber's salt is returned to the black liquor and a concentrated Cl and K solution is purged. Fujisaki et al. (2001) reported on results for the sixth mill (the Oji.s Kasugai mill in Japan) to adopt this patented technology, known as Potassium

Removal Equipment. The system removes 90 % of Cl and 75 % of K, and has obtained 96.6 % recovery of Na_2SO_4. ERCO Worldwide developed a process based on evaporative crystallisation known as the chloride removal process (CRP). The first CRP unit was installed as part of the bleach filtrate recycle (BFR) technology demonstration facilities in Canton, North Carolina. CRP uses forced circulation evaporation to concentrate the dissolved ESP catch. Sodium sulphate crystallises at saturation, is removed by filtration and returned to the black liquor. Cl and K are purged as a low-volume brine wastewater. Other CRP units have since been installed at mills to improve recovery boiler performance where no bleaching filtrate recovery is practiced. CRP units or developments of this system have been installed at Visy Tumut, NSW, International Paper Eastover, SC, USA and Smurfit-Stone, Hopewell, VA, USA.

Kværner has developed a leaching system. In this system, a centrifuge is used to separate Na_2SO_4. Aracruz, Brazil BEKP mill is using this leaching system. Also this system has been installed in Chile and China.

Other processes for removing Cl and K from the ESP catch have been developed (Stratton et al. 2003). An example is the Precipitator Dust Purification process that was jointly developed by Paprican and ProSep Technologies, Inc. of Canada. This process uses ion exchange technology to generate a purged stream rich in NaCl and a recovered stream rich in Na_2CO_3 and Na_2SO_4. Precipitator dust is dissolved in water and filtered prior to the ion exchange step. Water is used to regenerate the ion exchange resin. Studies using precipitator dust from two mills showed efficiencies of more than 95 % for Cl removal and 85 % for Na recovery, however, K removal efficiency was insignificant. The recovered stream would be directed to the black liquor evaporators (Jemaa et al. 1999).

Another method to Cl purging is to promote the formation of hydrogen chloride gas which will pass through the ESP where it can be scrubbed from the flue gas. Sulphur dioxide reacts with NaCl in the flue gas to give HCl gas. Sulphur dioxide concentrations generally limit the amount of NaCl converted to HCl, but mills that operate at high liquor sulphidity may have most of the Cl load in HCl form. A number of Scandinavian mills operate in this manner, utilising scrubbers for SO_2 control. In these mills, the scrubber wastewater may serve as a significant Cl purge.

4.26 Water Recycling/Reuse

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 chemicals toxic to marine life.

The driving forces responsible for waste water recycling in pulp and paper industry are the high cost of fresh water, inclination of the industry towards environment friendly process, discharge norms lay down by regulatory authorities, community

Table 4.38 Advantages of waste water recycling

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

Table 4.39 Water conservation measures adopted in the pulp mill

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 tower and vats and shower sprays in the preceding stage

Based on Bajpai (2008b)

perception and high cost of secondary effluent treatment process (Bajpai 2008b). The advantages of waste water recycling are shown in Table 4.38.

Industry has several options with respect to minimizing the use of fresh water. 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 upon the category and scale of operations.

The water consumption can be reduced to a great extent by making minor modifications in the process which 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 towards this goal has been going on for more than three decades. Some of the simple water conservation measures in the pulp mill are shown in Table 4.39.

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 has 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 counter current 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, 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 (Anon 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 sulphate pulp. The Wisaforest pulp mill of UPM-Kymmene Corporation has started to use bleach plant filtrate for post-oxygen washing on fibre line 1 (Siltala and Winberg 1999).

Recycle loops observed in market bleached Kraft mills are described below:

- 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 brownstock 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 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 make-up.
- Liquor evaporator condensates are utilized for boiler feed water make-up (clean condensates), causticizing mud washers, lime-kiln scrubbers, dreg washing, and wood yard requirements.

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

Wood preparation: All wood flumes utilize recycled waters. Wet debarking has typically been eliminated. Remaining water requirements are met with process wastewater.

Washing: Brown stock washing is typically accomplished entirely with waste water from the evaporators and turpentine decanter underflow from pulping.

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.

Cleaning/Refining: Stock preparation waters are met primarily with machine and/or press section white water.

Drying: Cooling water for drum bearing lubrication system, air conditioning, etc. is either recycled via an evaporative cooler or is returned to freshwater reservoirs.

Liquor Evaporation: Condenser cooling water is either recycled via an evaporative cooler or returned to freshwater reservoirs.

Causticizing: Water requirements for mud washing, dregs filter showers, and lime kiln scrubbe rs are supplied by other sub process waste streams. Cooling water is returned to freshwater reservoirs.

The kappa number of the pulp going to the bleach plant can be reduced by using chemical additives, such as anthraquinone and polysulphides, or by using modified cooking techniques such as modified continuous cooking (MCC) and extended MCC, isothermal cooking (ITC™), black liquor impregnation (BLI), LoSolids™ cooking, 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 liquor cycle. These technologies have reduced the bleach plant effluent considerably.

The chemicals applied to pulp in the oxygen delignification and ozone stages and the material removed from the pulp in the brown stock washing area, are compatible with the black liquor recovery system. Therefore, filtrate from the wash press after the ozone stage is utilized as full counter-current washing through the post-oxygen wash press and brown stock washers, and sent to the recovery area to be evaporated and burnt in the recovery boiler.

Campo and Marques (2009) reported in a retrofitted bleach plant that is designed to process bleached softwood pulp or, alternatively, bleached hardwood pulp with low effluent flow and load, the total bleaching plant effluent volume is maintained at a very low level, approximately 6–8 m^3/ADt in ECF and 4–6 m^3/ADt in TCF, with COD about 17 and 18 kg/ADt, respectively. A modern ECF-bleaching plant with countercurrent washing system normally uses a waste water flow in the order of magnitude of 15–20 m^3/ADt. Further closure of the bleach plant filtrates should be based on the balances of 'non process elements' (NPE) including chloride and potassium, the sodium/sulphur balance and the energy balance of the mill.

The extent of closing water circuits in the bleach plant depends also on the quality of the fresh water source, the type, number and capacity of washing equipment, designed existing bleaching sequence and due to its cross-media effects in other process areas, also in the capacity of the recovery boiler part of the mill to deal with possible problems (example K and Cl accumulation in the recovery boiler). A prerequisite for partial bleach plant closure is a sufficient capacity in evaporators and recovery boiler. It should be noted that the evaporation of bleach plant effluents is easier to apply in case of TCF bleaching. For safety reasons, in ECF bleaching there is an elevated risk of chloride corrosion in the recovery boiler with the level of development.

Södra Cell mills in Mönsterås, Mörrum and Värö (SE), Celtejo mill, (PT), Mercer Stendal and Rosenthal kraft pulp mill (DE), many others are practicing process water recycling (European Commission 2001).

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 (European Commission 2013). After a careful analysis of the water flows in the mill, and with the help of mathematical optimization through 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 fibre 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.

Using wash presses at the brown stock increases the pulp consistency to more than 30 % and the filtrate can be taken into the liquor cycle for recovery. It will also require less water to wash the brown stock. In fact, use of wash presses compared to filters in bleach plants can reduce effluent by about 50 % without any closure (Germguard and Steffes 1996). For example, the Advance Agro mill in Thailand uses presses in a three-stage bleach plant. The bleach plant effluent volume is reported to be 8–9 m^3 per tonne compared to 20–25 m^3 per tonne in similar plants using vacuum washers. Wash presses have a further benefit in that they use a limited amount of wash water, which increases the potential to reduce effluents. In addition, a press can restrict the amount of heat carryover between stages, which would significantly improve process conditions for a following ozone stage, which requires low temperatures.

As water is used, collected and reused in the papermaking process, the concentration through filtration of suspended solids increases. This can be detrimental to the paper product or process of papermaking. Filtration, or the physical separation of the unwanted particles from the water, is necessary if the water is to be reused in the paper mill. Various filtration components allow papermakers to use filtration to conserve water through the reuse of waters used in the papermaking process. The choice of filter type (strainers, pressure filters, gravity filters, save-all), filter media, filter location and filter maintenance programmes are critical to successful water reuse (Walter 1996). Machine backwater can be reused in high-pressure paper machine showers. The choice of showers to use clarified white water must take into account the payback risks of plugging nozzles and of the ‘plating out’ of solids on machine surfaces. Barrier filtration technology is limited to removing particles larger than 75 μm while dissolved air flotation (DAF) clarifiers are prone to upset by fluctuations in the flow rate and the suspended solids load. This tends to restrict the use of clarified white water to low-risk showers. In a linerboard mill, using white water in low risk and medium risk showers could achieve 33 % and 48 % in savings, respectively (McGowan 2002). Using the Petax fine filtration system developed by Kadant, fines and high solids can be removed in a single stage. Inlet concentrations of up to 2000 parts per million (ppm) can be treated without chemicals, without a vacuum drop leg and without fibre sweetener stock. Filtrate passes through disk filter media into a hollow shaft, which directs the filtrate to a hollow screen. Fines and solids are trapped on the exterior of the filter screen. Trapped debris is removed in three cleaning stages, with contaminants drawn out of the system by two positive displacement pumps. The recovered clear water is used in machine showers.

4.27 Primary, Secondary and Tertiary Waste Treatment

4.27.1 Primary Treatment

For most paper mills, this measure is not considered as a standalone technique but as a pretreatment. Pretreatment is usually carried out ahead of biological treatment in order to facilitate and improve the treatment process. In some special cases where the organic load is too low for efficient biological treatment, primary treatment may be the only waste water treatment.

Primary treatment primarily aims at:

- Avoiding peaks in pollution load, temperature or flows of the influent of a waste water treatment plant, thus protecting the later biological treatment
- Initially reducing the pollution load allowing for a more efficient biological treatment with generation of less sludge

Primary waste water treatment consists of physical-chemical treatment. It consists of:

- Equalisation,
- neutralization
- Sedimentation
- Flotation
- Filtration

In equalisation tank, the inflow is collected, mixed and intermediately stored and thus peaks are leveled. Suspended solids – fibres, bark particles, and organic material such as fillers – are removed by mechanical means (sedimentation, flotation and filtration). Coagulants or flocculants can be added in order to enhance the clarification and separation of some suspended solids, colloidals and certain dissolved substances,. Achieved environmental benefits are reduction of pollution load, especially total suspended solids (TSS). Primary waste water treatment methods are described below:

- Coarse screening is carried out for removing larger objects and sand, which may cause damage to the subsequent equipment
- Equalisation and spill collection are required for effluents with large variations as regards flow and content of pollutants. Such variations may disturb the function of the subsequent treatment processes, especially biological processes. A retention time of 4 h in the equalisation basin can be taken as an indication for appropriate design. However, the appropriate retention time of the equalisation tank depends on fluctuations in water quality.

- Primary or mechanical treatment: Sedimentation is carried out for the removal of suspended solids (SS), such as fibres, 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. Also, microfilters as a first stage before the clarifier are used, which allow for recovering of some fibres. Microflotation can also be used for primary clarification. Some smaller mills use primary treatment by means of filtration as the only waste water treatment. The particles, settling to the bottom of the primary clarifier form a sludge, which has to be removed. This is obtained by pumping in circular clarifiers in combination with bottom scraping. The sludge is usually low in dry solid (DS) content, approximately 1–2 %, and has to be thickened and dewatered before final disposal.

4.27.2 Secondary Waste Water Treatment

4.27.2.1 Aerobic Treatment

Pulp and paper mill effluents are mostly treated with aerobic methods. The commonly used aerobic treatment methods are aerated lagoon and activated sludge process (Nesaratnam 1998). Biofilm systems (such as moving bed biofilm reactors (MBBR) or membrane bioreactors (MBR) are also being used. Aerobic biological waste water treatment consumes energy (example for aerators and pumps) and generates sludge that normally requires treatment before utilisation or disposal. Some biological treatment plants in the pulp industry have detected Legionella bacteria. The issue should be taken care of by operators in cooperation with the competent authorities in order to reduce and control the dispersion of these bacteria. The environmental benefits achieved are reduction of emissions of organic matter (COD, BOD), AOX, phosphorus, nitrogen and chelating agents to water.

Aerated lagoons have been used for a long time in many pulp and paper mills for medium level removal of effluent contaminants. An aerated lagoon or aerated basin is a holding and/or treatment pond provided with artificial aeration to promote the biological oxidation of wastewaters. In aerated lagoon, the reduction of pollutants is lesser. 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. Aerated lagoons have a large volume; the residence times for the effluent is 3–20 days. The micro-organisms grow in suspension in the bulk of liquid, reaching in the lagoon relatively low solids concentration, 100–300 mg/l. The growth of micro-organisms requires oxygen, which is provided almost exclusively by mechanical aeration equipment. Surface turbine aerators are the most common aeration units. However, in deep lagoons also bottom aerators with self-induced or compressed air feed are also used. Aeration equipment provides also mixing required to keep solids in suspension and enhance microbial action. Aerated lagoons require large area and volume and are constructed as 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 removed seldom, once in 1–10 years.

Activated sludge plants are widely used in the pulp and paper industry. As a rough estimate, the activated sludge process is used in 60–75 % of all the biological effluent treatment plants in this industry and is also the most common waste water treatment used in recently built plants. Generally, the activated sludge process – or comparable techniques such as moving bed biofilm reactors – achieve high treatment efficiencies. However, the biomass is vulnerable to disturbances and operational instability. Therefore, operators usually make provisions that peak loads or flows or some toxic waste water streams be kept away from the biomass of the aerated basin. The activated sludge plant consists of aeration basin and the secondary clarifier -sedimentation basin. The effluent is treated in the aeration basin, with a culture of micro-organisms (the activated sludge), which are present in a high concentration. The sludge is separated from the water in the clarifier. The main part of the sludge is recycled to the aeration basin, which is important 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 is provided to the aeration basin by mechanical aeration equipment. Various types of aerators listed below are in use:

- Surface aerators
- Submerged turbine aerators
- Fine bubble aerators
- Jet aerators

The last three aerators require compressed air from blowers or compressors. A large number of process and plant designs exist for the activated sludge process. These alternatives may vary in design of the aeration basin, the number of stages, the clarifier, the aeration equipment, and also the sludge recycling.

The basis of the moving bed biofilm reactor (MBBR) process is the biofilm carrier elements that are made from polyethylene. The elements provide a large protected surface area for the biofilm and optimal conditions for the bacteria culture to grow. The bacterial cultures digest the soluble organics, gradually mature, and slough from the media. The cultures form a natural floc that can be easily separated from the water.

Compact biological treatment effluent plants were developed during the last decade in order to reduce volumes and decrease energy consumption. This combines moving bed carriers with activated sludge (BAS). The advantage of the biofilm carrier is that a large amount of biomass is staying on the carrier and does not have to be circulated via a sedimentation chamber. The advantage of this reactor compared with fixed beds is that there is no risk of plugging. This technology reduces the retention time by at least 50 % compared with traditional activated sludge plants.

The smaller volume makes it possible to build the biological treatment plants closer to the production line thus saving energy and costs. The reduction of COD is similar in all different types of treatment plants with activated sludge, but the sludge production is lower than in activated sludge plants when sludge is decomposed in the last stage of the BAS plant (example BAS 0.15 kg SS compared to long term activated sludge treatment plant (LAS) 0.3 kg SS/kg reduced COD (reference Södra mills)) (European Commission 2013). Due to anoxic conditions in the growing biomass, reduction of chlorate is high, 95–100 % and due to the compact volume (BAS 23 kWh/ADT compared to LAS 0.33 kWh/ADt), BAS treatment plants use less energy than other treatment plants. However, these compact systems are sensitive to lack of nutrients as the retention time is short. Therefore, these systems are operated with a nutrient surplus, leading to higher emissions of phosphorus and nitrogen.

Membrane bioreactor (MBR) generally consists of an aerated bioreactor, similar to activated sludge process, combined with a membrane process to separate the biomass from the effluent. Two basic MBR configurations exist:

- Membranes are immersed in the reactor and are an integral part of the biological reactor (internal/submerged)
- Membranes are a separate unit process following the biological reactor (external/sidestream).

The cleared filtrate from the membrane stage can be reused in the process and the separated biomass is recirculated to the bioreactor. The high quality of the filtrate makes the MBR technology best suited for use as internal water circuit treatment. To avoid solids accumulation on the membrane surface, the membrane system requires in defined time intervals a mechanical or chemical cleaning. This is normally done fully automatic and carried out directly in the MBR basin (no removal of membranes is necessary).

4.27.2.2 Anaerobic Treatment

In anaerobic biological waste water treatment, the biologically degradable load is reduced in absence of oxygen by digestion by microorganisms mainly generating methane and carbon dioxide. Anaerobic pretreatment reduces the organic pollution load of waste water, reduces the excess sludge generated in comparison to standalone aerobic treatment and utilises the energetic content inherent in the organic pollution load (biogas production) (Bajpai 2000). The volume of biogas produced during anaerobic degradation ranges from 400 to 600 m^3/tonne COD removed and consists of methane (60–75 %), carbon dioxide (20–35 %) and small amounts of hydrogen sulphide. Before being used as fuel in in-mill power plants as substitution of fossil fuels, the biogas is desulphurised. Otherwise, corrosion problems and higher sulphur dioxide emission in the power plant occur.

The main reactor types used are (Bajpai 2000):

- Fixed-bed reactor
- Sludge contact process
- Anaerobic upflow sludge blanket (UASB)
- Expanded granular sludge blanket (EGSB)
- Internal circulation (IC) reactors.

Sludge particles are kept fluidised by the up-flowing influent in UASB and EGSB reactors whereas in IC reactors, the gas produced in the system drives the circulation and mixing of liquid and solids in the reactor. The purpose of the different reactor concepts is to ensure a high concentration of biomass within the reactors. This is accomplished either by recycling washed out biomass after settling in an external separator (contact reactor system), by attaching the biomass to a supporting media within the reactor (fixed-bed reactor) or through auto-immobilisation producing granular biomass (UASB and EGSB reactor). The reactors can be operated as single units or as modular combined units.

Combined anaerobic/aerobic treatment plants have proved themselves to be more stable systems with respect to changing COD loads and toxic or inhibiting substances in the process water as compared to standalone aerobic treatment plants. For an economic application of anaerobic techniques as a first stage of biological waste water treatment, the COD concentration of the process water should not be less than 1000–2000 mg/l. Depending on the design of the anaerobic reactor suspended solids in concentrations above 200–500 mg/l could cause problems in anaerobic systems, particularly 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 with new pellets from other UASB reactors in order to keep the reactor in effective operation. The anaerobic pretreatment significantly reduces the tendency for developing bulky sludge in the subsequent aerobic stage. In standalone and well designed aerobic plants, the energy demand for 1 tonne COD removed amounts to 500–600 kWh whereas 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 (European Commission 2013).

4.27.3 Tertiary Treatment

Tertiary treatment is performed to reduce the emissions of suspended solids, partly non-biodegradable dissolved COD matter and phosphorus. It is used when further removal of organic substances, nitrogen or phosphorus is required. The reduction of suspended matter emissions also reduces the nutrient emissions bound thereto. A rather high amount of chemical sludge is produced. This sludge is more difficult to dewater and handle than biosludge. Aluminium or iron residues can be measured in low concentrations in the treated effluents after chemical precipitation. This treatment can be a reasonable solution when the waste water load changes significantly during different seasons and the performance of the secondary treatment (example.

an aerated lagoon) is lower compared with a well designed and operated activated sludge plant. It is also used to improve the efficiency of waste water treatment (example in case of aerated lagoons). Low reduction efficiencies for phosphorus and COD of aerated lagoons in wintertime can be improved (PARCOM 1994; SEPA-Report 4713-2 1997b).

SE Varkaus mill, tertiary treatment achieved the following reductions (Nurmesniemi 2010): TSS 55 %; COD 35 %; Phosphorus 60 %; Nitrogen 50 %. At the Varkaus Mill, all sludges are mixed before being dewatered with a screw press and the dried sludge is incinerated at the mill's own power plant. At the SE Varkaus mill, investment cost of tertiary treatment after the aerated lagoon was lower compared with the upgrading of the aerated lagoon to the activated sludge plant (Nurmesniemi 2010).

Biological treatment plus chemical flotation of waste water from the manufacturing of kraft pulp is used at some plants in Sweden, example, Skoghall, Billingfors, Bäckhammar or Iggesund. Several mills in Finland also use tertiary treatment with chemical flotation (example. SE Varkaus).

References

Agin SA, Svensson Å (1990) Fibre losses – economic consequences for the wood yard processes. In: Proceedings of the 24th Eucepa conference, Stockholm, pp 47–55

Ahluwalia MR, Coffey JM, Norris A (1992) Emerging technology in kraft pulping with digester additives. In: CPPA Spring conference proceedings, Canada, p 1

Albert RJ (1995) Worldwide status of effluent-free technology for bleached kraft pulp production. In: Proceedings if the international non-chlorine bleaching conference, Amelia Island, FL, March, Paper 9–2

Albert RJ (1997) Effluent-free pulp mill possible with existing fiberline equipment. In: Advances in bleaching technology. Miller Freeman Books, San Francisco, p 133

Alejandro M, Saldivia G (2003) Two-stage O_2 delignification system cuts mill's chemical use**.** Boosts Pulp Qual January/February, PaperAge, pp 18–24

Alliance for Environmental Technology (AET) (2002a) Trends in world bleached chemical pulp production: 1990–2001

Alliance for Environmental Technology (AET) (2002b) Eco-system recovery: lifting of fish consumption advisories for dioxin downstream of US Pulp Mills – 2002. Update

Alliance for Environmental Technology (AET) (2007) Trends in world bleached chemical pulp production: 1990–2007. Alliance for Environmental Technology, Washington, DC

Alliance for Environmental Technology (AET) (2008a) ECF: the sustainable technology, quality paper clean environment. Alliance for Environmental Technology, Washington, DC, 2008. Available online at http://www.aet.org/epp/brochure_0806.pdf

Alliance for Environmental Technology (AET) (2008b) Trends in world bleached chemical pulp production, 1990–2007, Alliance for Environmental Technology, Washington, DC, 2008. Available online at http://www.aet.org/science_of_ecf/eco_risk/2008_pulp.html

Alliance for Environmental Technology (AET) (2013) Trends in World Bleached Chemical Pulp Production: 1990–2012 www.aet.org/science_of_ecf/eco_risk/2013_pulp.html

Allison RW (1979) Effect of ozone on high-temperature thermo-mechanical pulp. Appita J 32(4):279–284

Allison RW (1980) Low energy pulping through ozone modification. Appita J 34(3):197–204

Amendola GA, Vice K, McCubbin N (1996) Design considerations for cost effective kraft and sulfite pulping liquor spill control systems. In: 1996 Tappi minimum effluent mills symposium proceedings. Tappi Press, Atlanta.

American Forest & Paper Assn (AFPA) (1988) Kraft recovery boiler physical and chemical processes, 1988, Textbook sponsored and published by AF&PA. Washington, DC

Aminoff H (1979) A mechanism for the delignifying effect of the anthraquinone in soda pulping. Pap Puu 61(6):29

Andbacka S (1991) Experiences of modified continuous cooking. Presentation at the Kamyr symposium in Portugal, April 1991

Andbacka S (1998) The importance of washing in oxygen delignification and TCF bleaching. Pulp Pap Can 99(3):57–60

Andbacka S, Svanberg J (1997) Isothermal cooking and pulp washing in a modern fiber line. In: 51th Appita general conference, proceedings 1, Melbourne, Australia

Anderson JR (1992) Hydrogen peroxide use in chemical pulp bleaching. In: Tappi bleach plant operations short course notes. Tappi Press, Atlanta, p 123

Anderson JR, Amini B (1996) Hydrogen peroxide bleaching. In: Dence CW, Reeve DW (eds) Pulp bleaching – principles and practice. Tappi Press, Atlanta, p 411

Andrew J, Chirat C, Mortha G, Grzeskowiak V (2008) Modified ECF bleaching sequences for South African hardwood kraft pulps. In: International pulp bleaching conference, Quebec City, QC, Canada, 2–5 June 2008, pp 55–60

Andrews DH, Singh RP (1979) Peroxide bleaching. In: Singh RP (ed) The bleaching of pulp, 3rd edn. Tappi Press, Atlanta, pp 211–253

Annergren G, Rydholm SA, Vardheim S (1963) Influence of raw material and pulping process on the chemical composition and physical properties of paper pulps. Sven Pap 66(6):196–210

Annola A, Hynninen P, Henricson K (1995) Effect of condensate use on bleaching. Pap Ja Puu 77(3)

Anonymous (1997) Closed loop bleaching'. UpTimes no. 1, 1997, p 8

Arenander S, Wahren D (1983) Impulse drying adds new dimension to water removal. Tappi J 66(9):123–126

Arpalahti O, Engdahl H, Jäntti J, Kiiskilä E, Liiri O, Pekkinen J, Puumalainen R, Sankala H, Vehmaan-Kreula J (2000) Chemical pulping, white liquor preparation. In: Gullichsen J. Fogelholm C-J (ed) Papermaking science and technology, book 6B. Gummerus Printing, Jyväskylä, pp B178–B202

Aurell R, Hartler N (1963) Sulphate cooking with the addition of reducing agents. Part III. The effect of sodium borohydride. Tappi 46(4):209–215

Axegård P (1999) Kretsloppsanpassad massafabrik-Slutrapport, KAM 1 1996–1999, KAMrapport A31, Stiftelsen för Miljöstrategisk forskning

Axegård P, Norden S, Teder A (1978) Production of pulp for bleaching – some principles. Sven Pap 81(4):97–100, 104

Axegård P, Carey J, Folke J, Gleadow P, Gullichsen J, Pryke DC, Reeve DW, Swan B, Uloth V (2003) Minimum -impact mills: issues and challenges. In: Stuthridge T, van den Hueval MR (eds)

Bajpai P (2000) Treatment of pulp and paper mill effluents with anaerobic technology. Pira International, Leatherhead

Bajpai P (2008a) Chemical recovery in pulp and paper making. PIRA International, Leatherhead, 166 pages

Bajpai P (2008b) Water recovery in pulp and paper making. PIRA International, Leatherhead

Bajpai (2010) Environmentally friendly production of pulp and paper. Wiley, New York

Bajpai P (2012a) Biotechnology in pulp and paper processing. Springer, New York, 412 pp

Bajpai P (2012b) Environmentally benign approaches for pulp bleaching, 2nd edn, Elsevier, London

Bajpai P, Bajpai PK (1999) Recycling of process water in a closed mill systems – an introduction. ISBN 1 85802 277 0, Pira International UK, 104 pages

Bajpai P, Kumar S, Mishra SP, Mishra OP, Bajpai PK (2005) Improving digester performance through the use of surfactants and AQ. IPPTA Conv Issue 43–53

Barratt KB (1990) Kraft pulping for the 90s environment. Paper presented at Tappi 90 conference held 5–8 March, 1990 at Atlanta, GA, USA, pp 95–102

Beca AMEC (2004) Study report: independent advice on the development of environmental guidelines for any new Bleached Eucalypt Kraft Pulp Mill in Tasmania, prepared for the Resource Planning and Development Commission, Tasmania, Australia

Beca AMEC (2006) Review of ECF and TCF bleaching processes and specific issues raised in the WWF report on Arauco Valdivia. Prepared for Resource Planning and Development Commission, Tasmania, Australia. May 2006

Bergnor G, Dahlman O (1998) Influence on pulp quality during the removal of hexenuronic acids In: Proceedings international pulp bleaching conference, Helsinki, Finland, p 185

Bergnor-Gidnert E (2006) STFI Pac kforsk report, February, 2006 (in Swedish)

Berry R (1996) Oxidative alkaline extraction. In: Dence CW, Reeve DW (eds) Pulp bleaching – principles and practice. Tappi Press, Atlanta, pp 291–320

Berthold F, Lindström ME (1997) Polysulfide addition as a means to increase delignification in kraft pulping. Nord Pulp Pap Res J 12(4):230

Bérubé PR, Hall ER (2000) Removal of methanol from evaporator condensate using a high temperature membrane bioreactor: determination of optimal operating temperature and system costs. Pulp Pap Can 101(3):54–58

Björk M, Sjögren, Tomas, Lundin T Rickards H, Kochesfahani, SH (2005) Partial borate autocausticizing trial increases capacity at Swedish mill, Tappi J 4(9):15–19

Blackwell BR, MacKay WB, Murray FE, Oldham WK (1979) Review of kraft foul condensates, sources, quantities, chemical composition, and environmental effects. Tappi J 62(10):33–37

Bokström M, Nordén S (1998) Extended oxygen delignification. In: Proceedings of the 1998 international pulp bleaching conference, Helsinki, Finland

Boman R, Reeves R, Nordgren B (1995) Mills improve bleach results with pressurized peroxide. Pulp Pap 69(10):121–125

Bonsu AK, Marois J, Rowbottom RS (1986) Standby wet scrubber for kraft digester blow and relief gases. Pulp Paper Can 87(8):T318-T323 (August 1986)

Borchardt JK, Biancalana RP, Mahoney CL (1997) Improved deresination agents: laboratory and mill results, In: Proceedings of the 1997 Tappi pulping conference, TAPPI Press, Atlanta, pp 395–413

Botnia Rauma (2009) Air emissions – Botnia Rauma mill. Presentation given during a mission to Finland, 23.02.2009,

Bouchard J, Maine C, Berry RM (1996) Kraft pulp bleaching using dimethyldioxirane: stability of the oxidants. Can J Chem 74(2):232

Bounicore A, Wayne TD (1992) Air pollution engineering manual. Van Nostrand Reinhold, New York

Bowen IJ (1990) Overview of emerging technologies in pulping and bleaching. Tappi J 73(9):205–217

Brännland R, Nordén S, Lindström LA (1990) Implementation in full scale – the next step for prenox. Tappi I 73(5):231–237

Bräuer P, Großalber J, Münster H, Zhang X, Nagalla RN (2012) China is steaming ahead with high-yield pulping, Success story of Chinese paper and board industry with the use of mechanical pulping, What can Asia learn from this, http://papermart.in/2012/09/28/china-is-steaming-ahead-with-high-yield-pulping-success-story-of-chinese-paper-and-board-industry-with-the-use-of-mechanical-pulping-what-can-asia-learn-from-this

Breed D, Shackford LD, Pereira ER, Colodette JL (1995) Cost-effective retrofit of existing bleach plants to ECF and TCF bleached pulp production using a novel peroxide bleaching process. In: 1995 pulping conference, Chicago, IL, USA, 1–5 October, 1995, Book 2, pp 779–788

Bright D, Hodson P, Lehtinen, K-J, Mckague B, Rodgers J, Solomon K (2003) Evaluation of ecological risks associated with the use of chlorine dioxide for the bleaching of pulp: scientific progress since 1993. In: T Stuthridge, van den Hueval MR, Marvin NA, Slade AH, Gifford J (eds) Environmental impacts of pulp and paper waste streams, SETAC Press, Pensacola

Brogdon BN, Hart PW (2012) Chapter 10: Peroxide bleaching. In: Hart PW, Rudie AW (eds) Bleaching of pulp, 5th edn. Tappi Press, Atlanta, pp 273–308

Brown C, Landälv I (2001) The chemrec black liquor recovery technology – a status report. In: International chemical recovery conference, Whistler, Canada, 11–14 June 2001

Buchert J, Teleman A, Harjunpaa V, Tenkanen M, Viikari L, Vuorinen T (1995) Effect of cooking and bleaching on the structure of xylan in conventional pine kraft pulp. Tappi J 78(11):125

Buchert J, Tenkanen M, Tamminen T (2001) Characterization of carboxylic acids during kraft and Superbatch pulping. Tappi J 84(4):1

Bujanovic B, Cameron J, Yilgor N (2003) Comparative studies of kraft and kraft-borate pulping of black spruce. J Pulp Pap Sci 29(6):190–196

Burgess T (1993) The basics of foul condensate stripping. In: Proceedings of the 1993 kraft recovery operations short course. Tappi J 137–146

Campo R, Marques P (2009) Celtejo plays in the top division. Results Pulp Pap 3:32–34

Cannell E, Cockram R (2000) The future of BCTMP. Pulp Pap 74(5):61–76

Canovas RV, Maples GE (1995) Bleach plant closure with the BFR™ process. In: 1995 nonchlorine bleaching conference proceedings. Orlando, Florida

Carre G, Wennerström M (2005) Ozone bleaching – an established technology. IPBC, Stockholm, pp 144–149

Carreira HJM, Loureiro PEG, Graca M, Carvalho MGVS, Evtuguinet DV (2012) Reductive degradation of residual chromophores in kraft pulp with sodium dithionite. Tappi J 11(3):59–67

Carter DN, McKenzie DG, Johnson AP, Idner K (1997) Performance parameters of oxygen delignification. TAPPI J 80(10):111–117

Chai XS, Luo Q, Yoon SH, Zhu JY (2001) The fate of hexanuronic acid groups during kraft pulping of hardwoods. J Pulp Pap Sci 27(12):403

Chandra B (1997) Effluent minimization – a little water goes a long way. Tappi J 80(12):37–42

Chemrec (2012) A gasification technology inherently more efficient. Retrieved on April 10, 2012. Available at: http://www.chemrec.se/

Chen CI (1990) Process for producing kraft pulp for paper using nonionic surface active agents to improve pulp yield, U.S. Patent 4,952,277

Chen GC (1994) Application of a surfactant as a kraft pulping additive. Tappi 77(2):125–128

Cheremisinoff NP, Rosenfeld PE (2010) Handbook of pollution prevention and cleaner production vol. 2: best practices in the wood and paper industries, 1st edn. Elsevier, New York

Chirat C, Lachenal D (1994) Minimizing pulp degradation during totally chlorine free bleaching sequences including an ozone stage. In: 1994 international pulp bleaching conference papers. Canadian Pulp and Paper Association, Montreal

Chirat C, Lachenal D (1997) Pulp producers race to keep up with technology. In: Pate KL (ed) Advances in bleaching technology. Miller Freeman Books, San Francisco, p 20

Chirat C, Nyangiro D, Struga B, Lachenal D (2005) The use of ozone on high kappa softwood and hardwood kraft pulps to improve pulp yield. IPBC, Stockholm, pp 74–80

Chirat C (2007). Proceedings of the EFPG days 2007, Grenoble, France

Cloutier JN, Lecourt M, Petit-Conil M (2009) Ozonisation of TMP – Part I – direct ozone injection in the eye of the secondary refiner In: PACWEST conference, Kamloops, BC, Canada, 10 pages

Cloutier JN, Lecourt, M, Petit-Conil M (2010) Ozonation of TMP – Part II – interstage treatment of primary TMP in a dedicated reactor In: PACWEST conference, Kamloops, BC, Canada, 9 pages

Colodette JL, Campos AS, Gomide JL (1990) Attempts to use white liquor as the source of alkali in the oxygen delignification of eucalypt kraft pulp. In: 1990 Tappi oxygen delignification symposium notes. Tappi Press, Atlanta, p 145

Confederation of European Paper Industries (CEPI) (2009) CEPI Europe's pulp and paper industry in 2020 and beyond. Carta & Cartiere 14–18

Cooper CD, Alley FC (1986) Air pollution control: a design approach. Waveland Press, Prospect Heights

Costa MM, Colodette JL (2002) The effect of kraft pulp composition on its bleachability. In: TAPPI international pulp bleaching conference, 2002. Ortland, Oregon, USA

Courchene CE (1998) The tried, the true and the new – getting more pulp from chips – modifications to the kraft process for increased yield. In: Proceedings of the breaking the pulp yield barrier symposium, 1998. Tappi Press, Atlanta, pp 11–20

Croon I, Andrews DH (1971) Advances in oxygen bleaching, Part I. Demonstration of its feasibility and scope. Tappi 54(11):1892–1898

Crotogino RH, Poirier NA, Trinh DT (1987) The principles of pulp washing. Tappi J 70(6):95–103

Dallons VJ, Hoy DR, Messmer RA, Crawford RJ (1990) Chloroform formation and release from pulp bleaching. Results of field measurements. Tappi J 73(6):91–95

De Beer JG (1998) Potential for industrial energy efficiency Improvement in the long term. PhD thesis Utrecht University, Department of Science, Technology, and Society

de Choudens C, Monzie P (1978) Pâtes TMP. Traitement par l'ozone, Atip 32(9):350–359

DeCarrera R (2006) Quaterly technical progress report 20 demonstration of black liquor gasification at Big Island. Report 40850R20 http://www.gp.com/containerboard/mills/big/pdf/rpt40850R20.pdf (06-04-28)

DeMartini Nl (2010) Final summary report on nitrogen oxide emissions from Finnish pulp mills. Finnish Recovery Boiler Committee, 2010

Department of Justice (2012) Pulp and paper effluent regulations (SOR/92-269). Department of Justice, Government of Canada, Ottawa, ON, Canada, 2012. Available online at http://laws.justice.gc.ca/eng/SOR-92-269

Desprez F, Devenyns J, Troughton N (1993) One stage hydrogen peroxide full bleaching of previously delignified soft wood kraft pulp. In: Tappi pulping conference proceedings. Tappi Press, Atlanta, p. 443

Devenyns J, Chauveheid E (1997) Uronic acid and metal control. In: 9th international symposium on wood and pulping chemistry. Montreal, QC, Canada, pp M5-1

Devenyns J, Desprez FS, Troughton N (1993) Peroxygen bleaching and prebleaching technologies for step wise conversion from conventional chlorine bleaching via ECF to TCF. In: Tappi pulping conference proceedings. Tappi Press, Atlanta, p 341

Diaconescu V, Petrovan S (1976) Kinetics of sulfate pulping with addition of sodium borohydride. Cellul Chem Technol 10(3):357–378

Dimmel DR (1995) Electron-transfer reactions in pulping systems. (1). Theory and applicability to anthraquinone pulping, Institute of Paper Chemistry. J Wood Chem Technol 5(1):1–14

Dimmel DR, Schuller LF (1986) Structural/reactivity studies (II): reactions of lignin model compounds with pulping additives. J Wood Chem Technol 6(4):565

Dubé M, McLean R, MacLatchy D, Savage P (2000) Reverse osmosis treatment: effects on effluent quality. Pulp Pap Can 101:8

Durai-Swamy K, Mansour MN, Warren DW (1991) Pulsed combustion process for black liquor gasification, U.S. DOE report DOE/CE/40893-T1 (DE92003672)

Eckert B, Turpin D, Dunn J (2005) Improving fiber yield through borate autocausticizing, Improving fiber yield through borate autocausticizing, Tappi/Solut April 2005, pp 33–34

EIPPCB (2011) Assessment of the data collection on air emissions from European kraft pulp mills, February – April 2011, 2011. European Commission, Spain

Eiras KMM, Colodette JL (2003) Eucalyptus kraft pulp bleaching with chlorine dioxide at high temperature. JPPS 29(2):62–64

Ek M, Axegård P, Bergnor E, Ekholm U (1994) The role of metal ions in TCF-bleaching of softwood pulps. In: Tappi pulping conference proceedings. Tappi Press, Atlanta

Elaahi A, Lowitt HE (1988) The U.S. pulp and paper industry: an energy perspective. U.S. Department of Energy, Washington, DC

Emilsson K, Håkansson M, Danielsson G (1997) Extended stripping and usage of evaporator condensates at Varo Mill, Sweden. In: 1997 Tappi minimum effluent mills symposium proceedings. Tappi Press, Atlanta

Engstrom JH (1996) Black liquor impregnation and iso thermal cooking. Pap Asia 12(2):18–21

Environment Canada (1992a) Aquatic effects monitoring requirements. Report EPS 1/RM/18, Environment Canada, Ottawa, ON, Canada, 1992

Environment Canada (1992b) Reference method for the determination of polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in pulp and paper mill effluents, Report EPS 1/RM/19, Environment Canada, Ottawa, ON, Canada, 1992

Enz SM, Emmerling F (1987) North America's first fully integrated, medium. consistency oxygen delignification stage. Tappi J 70(6):105–112

EPA, NCASI (1995) Survey of recovery furnaces in the kraft pulp sector, carried out by NCASI in cooperation with EPA in 1994–1995

Eriksson E, Sjöström E (1968) The influence of acid groups on the physical properties of high-yield pulps. Tappi J 51(1):56

Ernerfeldt B, Södersten PA, Eriksson HO, Näsholm AS (1999) Bleach plant presses reduce chemical consumption. In: 6th international conference on newly available technologies, Stockholm

European Commission (2001) Integrated Pollution Prevention and Control (IPPC). Reference document on best available techniques in the pulp and paper industry. Institute for Prospective Technological Studies, Seville

European Commission (2013) Best Available Techniques (BAT) reference document for the production of pulp, paper and board. Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control). JOINT RESEARCH CENTRE, Institute for Prospective Technological Studies Sustainable Production and Consumption Unit European IPPC Bureau

Fatehi P, Malinen RO, Ni Y (2009) Removal of hexenuronic acid from eucalyptus kraft pulps during chlorine dioxide- and ozone-based ECF bleaching sequences. Appita 62(3):212–218

Finnish BAT Report (1997) The Finnish background report for the EC documentation of best available techniques for pulp and paper industry. The Finnsih environment 96, Ministry of Environment in Finland, Helsinki 1997, ISBN 952-11-0123-7

Fleming BI, Kubes GJ, MacLeod JM, Bolker HI (1978) Soda pulping with anthraquinone. A mechanism. Tappi 61(6):43

Ford M, Sharman P (1996) Performance of high yield hardwood pulp is investigated as it should be the choice of the future. Pulp Pap Int 38(10):29

FRBC (2010) NOx emissions from recovery boilers – why discrepancy between Finnish and Swedish values, Finnish Recovery Boiler Committee, 22.12.2010, 2010, p 12

Fujisaki A, Tateishi M, Baba Y, Arakawa Y (2001) Plugging prevention of recovery boiler by character improvement of the ash which used potassium removal equipment (part II). In: Proceedings of the international chemical recovery conference, Pulp and Paper Technical Association of Canada, Tampa

Fullerton TJ, Wright LJ (1984) Redox catalysis of alkaline pulping by organometallic complexes. Wood Chem Technol 4(1):61–74

Furtado FP, Evtugin DV, Gomes TM (2001) Effect of the acid stage in ECF bleaching of eucalyptus globulus kraft pulp bleachability and strength. Pulp Pap Can 102(12):93

Gabir S, Khristov T (1973) Kraft cooks of papyrus (*Cyperus papyrus* L.) stalks in the presence of sodium borohydride. Tselul Khartiya 4(6):12–18

Gavrilescu D (2005) Best practices in kraft pulping – benefits and costs. Environ Eng Manag J 4:29–46

Gebart R (2006) Improvement Potential in chemical pulping: black liquor gasification. In: Paper presented at the IEA-WBCSD workshop on energy efficient technologies and CO_2 reduction potentials in the pulp and paper industry, Paris, France

Gellerstedt G (2003) Condensation in kraft pulping. A reality?. In: 12th International Symposium on Wood and Pulping Chemistry (ISWPC) Madison, USA, June 9–12, 2004, Vol I, 1

Genco JM, van Heiningen A, Miller W (2012) Chapter 2: Oxygen delignification, the bleaching of pulp. In: Hart P, Rudie A (eds) TAPPI Press, Atlanta

Germer E, Metais A, Hostachy JC (2011) State-of-the-art industrial ozone bleaching. Tappsa J 6:30–37

Germguard U, Steffes F (1996) Pulp washing in a closed bleached plant. In: Proceedings of the Tappi 1996 minimum effluent mills symposium. Tappi Press, Atlanta, pp 115–118

Gleadow PL, Hastings C (1995) Closed cycle kraft ECF vs. TCF. In: Proceedings international non-chlorine bleaching conference, Amelia Island, FL, March, Paper 9–1

Gleadow PL,Vice K, Johnson AP, Sorenson DR, Hastings CR (1996) Mill applications of closed cycle technology. In: Proceedings international non-chlorine bleaching conference, Orlando, FL, March, Paper 11–3

Gomes da Silva Jr F, Duarte FA, Saco VM, dos Santos JT, Bassa A (2002) Ozone based ECF bleaching sequence for eucalyptus pulp: optimization studies. In: TAPPI International pulp bleaching conference. Portland, OR, USA

Gorski D, Engstrand P, Hill J, Johansson L (2009) Review: reduction of energy consumption in refining through mechanical pretreatment of wood chips. In: International mechanical pulping conference, Sundsvall

Gotlieb PM, Nutt WE, Miller SR, Macas TS (1994) Mill experience in high-consistency ozone bleaching of southern pine pulp. Tappi J 77(6):117–124

Govers T, Homer G, Scheeff D (1995) The cost of ozone-based ECF and TCF bleaching. In: AIR LIQUIDE/OZONIA ozone symposium, Helsingör, Denmark. http://perso.wanadoo.fr/govers/aecono/pulp_bleaching. (28–29 September 1995)

Goyal GC (ed) (1997) Anthraquinone pulping: a Tappi Press anthology of published papers, 1977–1996. Tappi Press, Atlanta

Goyal G, Jokela V, Munro FC (1994) Low kappa number pulping – mill experiences, In: 1994, Tappi pulping conference. Tappi Press, Atlanta, p 305

Grace TM, Timmer WM (1995) A comparison of alternative black liquor recovery technologies. In: Proceedings of the international chemical recovery conference, Toronto, pp B269 – 275

Gratzl JS (1980) The action mechanism of anthraquinone in alkaline pulping. EUCEPA symposium "The delignification methods of the future", Helsinki, paper 12

Gullichsen J (2000) Fiber line operations. In: Gullichsen J, Fogelholm C-J (eds) Chemical pulping – papermaking science and technology, Book 6A. Fapet Oy, Helsinki, Finland, p A19

Gullichsen J, Paulapuro H, Sundholm J (2000) (book editor), Papermaking science and technology, Book 5. Mechanical pulping, Fapet Oy, Helsinki, Finland

Gullichsen J, Ilmoniemi E, Kaasalainen H, Manninen TA (2009) Method for feeding high-consistency pulp to a formation support and high-consistency Headbox, WO 2009063135 (A1)

Håkansdotter L, Olm L (2002) Soda-AQ pulping of softwood, the influence of cooking parameters on the properties and bleachability. Pap Puu 84(1):43

Haller KH (1996) A decision in favor of ECF: what a decision in the German speaking area. In: Proceedings International Non-Chlorine Bleaching Conference, Orlando, FL

Hamm U, Gottshing L (2002) ECF and TCF bleached pulps: a comparison of their environmental impact. German Pulp and Paper Association VDP—INFOR project (No. 19)

Han Y, Law KN, Lanouette R (2008) Modification of jack pine TMP long fibers by alkaline peroxide –Part 1. Chemical characteristics of fibers and spent liquor. BioResources 3(3):870–880

Harazono K, Kondo R, Sakai K (1996) Bleaching of hardwood kraft pulp with manganese peroxidase from *Phanerochaete sordida* YK-624 without addition of $MnSO_4$. Appl Environ Microbiol 62(3):913–917

Hartler N (1959) Sulfate cooking with the addition of reducing agents. I. Preliminary report on the addition of sodium borohydride. Sven Pap 62:467

Hatton J (1987) Debarking of frozen wood. Tappi J 70(2):61–66

He Z, Wekesa M, Ni Y (2004a) Pulp properties and effluent characteristics from the Mg(OH)(2)-based peroxide bleaching process. Tappi J 3(12):27–31

He Z, Ni Y, Zhang E (2004b) Further understanding on the cationic demand of dissolved substances during peroxide bleaching of a spruce TMP. J Wood Chem Technol 24(2):153–168

He Z, Qian X, Ni Y (2006a) The tensile strength of bleached mechanical pulps from the Mg(OH)2-based and NaOH-based peroxide bleaching processes. J Pulp Pap Sci 32(1):47–52

He Z, Wekesa M, Ni Y (2006b) A comparative study of Mg(OH)(2)-based and NaOH-based peroxide bleaching of TMP: anionic trash formation and its impact on filler retention. Pulp Paper Can 107(3):29–32

Headley RL (1996) Pulp cooking developments focus on fiber yield, lower chemical use. Pulp Pap 70(10):49–57

Heimburger S, Thireault D, Boechler T (2002) International pulp bleaching conference. Tappi Press, Atlanta, p 271

Helander R, Nilsson B, Bohman G (1994) Developments and progress in ozone bleaching at the Skoghall mill. In: CPPA international pulp bleaching conference papers, CPPA, Montreal, p 289

Henricson K (1997) Ahlstrom machinery, AHLTM-stage. A new bleaching stage for kappa reduction and metal profile control, In: Emerging new technologies conference (March 1997), Orlando, USA

Hill J, Sabourn M, Johansson L, Aichinger J (2009) Enhancing fibre development at reduced energy consumption using TMP subprocesses and targeted chemcial application – pilot and commercial scale results, International Mechanical Pulping Conference, Sundsvall, Sweden, May 31–June 4

Hitchens D, Farrell F, Lindblom J, Triebswetter U (2001) The impact of Best Available Techniques (BAT) in the competitiveness of European industry. European Comission, report EUR 20133 EN. 120 pp

Hoddenbagh JA, Wilfing K, Miller K, Hardman D, Tran H, Bair C (2001) Borate autocausticizing – a cost effective technology. In: International chemical recovery conference, Whistler, Canada, 11–14 June 2001, pp 345–53

Holmbom B, Ekman R, Sjoholm R, Eckerman C, Thornton J (1991) Chemical-changes in peroxide bleaching of mechanical pulps. Papier 45(10A):16–22

Holton H (1977) Soda additive softwood pulping: a major new process. Pulp Pap Can 78(10):19

Homer G, Muguet M, Epiney M, Johnson S (1996) Oxygen, ozone, and chlorine dioxide. In: 82nd annual meeting, technical section, CPPA, Montréal, 1996

Hosoya S, Tomimura Y, Shimada K (1993) Acid treatment as one stage of non chlorine bleaching, In: 7th international symposium on wood and pulping chemistry, vol 1, Beijing, China, p 206

Hostachy JC (2009) Bagasse pulp bleaching with ozone: it's time to implement green bleaching practice paperex. In: 2009 – international technical conference 4-6th December 2009, New Delhi, India

Hostachy JC (2010a) Ozone-enhanced bleaching of softwood kraft pulp, Tappi J 9(8):16–23

Hostachy JC (2010b) Softwood pulp bleaching with ozone: a new concept to reduce the bleaching chemical cost by 25%, Appita 63(2):92–97

Hostachy JC (2010c) Use of ozone in chemical and high yield pulping processes: latest innovations maximizing efficiency and environmental performance. In: 64th Appita annual conference and exhibition, 18–21 April 2010, Melbourne, Australia, pp 349–354

Hostachy JC, Serfass R (2009) Ozone bleaching – state of the art and new developments www.otsil.net/…/ozone%20bleaching%20State%20of%20Art%20TECHNOLOGY%2…A. Wedeco report

Hsieh JS, Long PX, BaOsman A (2000) Kinetic study of ozone treatment on mechanical pulp. In: Proceedings from the 2000 Tappi pulping/process & product quality conference, Boston, DF MA, Paper 46

Huber E, Rank P, Rauscher JW, Williamson DF (1995) High black liquor solids firing at pope and talbot. In: Proceedings of the 1995 international chemical recovery pulping conference. TAPPI Press, Toronto.

Hupa (2005). Nitrogen oxide emissions from pulp mills and the factors affecting them – a summary of the current knowledge, Report for the Finnish Recovery Boiler Committee, 2005, p. 15

Hyoty PA, Ojala ST (1988) High solids black liquor combustion. Tappi J 71(1):108–111

Ibach S (1995). Conversion to High Solids Firing, Proceedings of the International Chemical Recovery Conference, TAPPI Press, Toronto, Ont., Apr. 1995

Imelainen K, Ekholm J, Kukkanen K, Pasola I (1989) A computer controlled recovery boiler burning high dry solids. Pulp Pap Can 90(4):15–20

International Energy Agency (IEA) (2009) Energy technology transitions for industry – strategies for the next industrial revolution. International Energy Agency (IEA), Paris

Istek A, Gonteki E (2009) Utilization of sodium borohydride ($NaBH_4$) in kraft pulping process. J Environ Biol 30(6):5–6

Jaakko Pöyry Consulting AB (1997) Energy conservation in the pulp and paper industry

Jaccard M, Willis Enterprises Associates (1996) Energy conservation potential in six Canadian industries. Natural Resources Canada, Ottawa

Jameel H, Gratzl J, Prasad DY, Chivikula S (1995) Extending delignification with AQ/polysulfide. Tappi J 78(9):151–160

Jamieson AG, Fossum G (1976) Influence of oxygen delignification on pulp yields. Appita 29(4):253–256

Jemaa N, Paleologou M, Thompson R, Richardson B, Brown C, Sheedy M (1999) Chloride removal from the kraft recovery boiler ESP dust using the precipitator dust purification (PDP) system. Pulp Pap Can 100:T219–T226

Jerschefske D (2012) China invests to meet booming paper demand. http://www.labelsandlabeling.com/news/features/china-invests-meet-booming-paper-demand

Jiang JE (1993) Extended delignification of Southern Pine with polysulfide and anthraquinone. In: Tappi pulping conference proceedings, Atlanta, November 14–18, pp 313–321

Jiang JE (1995) Extended delignification of southern pine with anthraquinone and polysulfide, Tappi J 78/2:126

Johansson B, Mjöberg J, Sandström P, Teder A (1984) Modified continuous kraft pulping – now a reality. Sven Pap 87(10):30–35

Johnson RW, Bird A (1991). CTMP in Fine Papers: Impact of CTMP on Permanence of Alkaline Papers, 1991 Papermakers conference proceedings, TAPPI Press: 267–273.

Johnson T, Gleadow P, Hastings C (1996) Pulping technologies for the 21st century – a North American view. Part 4 emerging technologies and mill closure. Appita 49(2):76–82

Johnson AP, Johnson BI, Gleadow P, Silva FA, Aquilar RM, Hsiang CJ, Araneda H (2008) 21st century fibrelines. In: Proceedings of the international bleaching conference, Quebec City, 2008

Jones AR (1983) How bleaching hardwood kraft pulp with oxygen affects the environment. Tappi J 66(12):42–43

Jönsson J (2011) Analysing different technology pathways for the pulp and paper industry in a European energy systems perspective. PhD thesis, Department of Energy and Environment, Chalmers University of Technology, Göteborg, Sweden

Jönsson J, Ruohonen P, Michel G, Berntsson T (2011) The potential for steam savings and implementation of different biorefinery concepts in Scandinavian integrated TMP and paper mills. Appl Therm Eng 31(13):2107–2114

Joseph JC, White DE (1996) The use of modeling in mill closure activities. In: 1996 Tappi minimum effluent mills symposium proceedings. Tappi Press, Atlanta

KAM Report A100 (2003) Ecocyclic pulp mill – “KAM”. Final report 1996–2002

Kapanen J, Kuusisto L (2002) A new brown stock washing optimization method for economical pulp production, TAPPSA APPW, 2002

Kappel J, Bräuer P, Kittel FP (1994) High consistency ozone bleaching technology. Tappi J 77(6):109

Karlström K (2009) Extended impregnation kraft cooking of softwood: effects on reject, yield, pulping uniformity and physical properties, Lic. thesis, Royal Institute of Technology (KTH), Stockholm, Sweden

Katofsky R, Consonni S, Larson ED (2003) A cost-benefit analysis of black liquor gasification combined cycle systems. In: Proceedings of the Tappi fall technical conference: engineering, pulping & PCE&I, Chicago, 22 p

Katsoulis DE (2002) A survey of applications of polyoxometalates. Chem Rev 98(1):359

Katz G (1993) Anthraquinone and anthraquinone-polysulfide pulping for extended delignification. In: Tappi pulping conference proceedings, Atlanta, November 14–18, pp 323–331

Katz S, Scallan AM (1983) Ozone and caustic soda treatments of mechanical pulp. TAPPI J 66(1):85–87

Kazymov D (2010) Biochemical modification of thermomechanical pulp fibers. Master’s degree program in chemical and process engineering. Lappeenranta University of Technology

Kibblewhite RP, Brookes D, Allison RW (1980) Effect of ozone on the fiber characteristics of thermomechanical pulps. Tappi J 63(4):133–136

Kignell JE (1989) Process for chemicals and energy recovery from waste liquors, U.S. Patent no. 4,808,264

Kiviaho I (1995) Optimizing oxygen delignification. In: Proceedings of the international non-chlorine bleaching conference, Amelia Island, FL, paper 2–2, p 12

Kleppe PJ, Kringstad K (1963) Sulfate pulping by the polysulfide process. II. Birch. Norsk Skogind 18(1):13

Kleppe PJ, Hm C, Eckert RC (1972) Delignification of high yield pulp with oxygen and alkali, I, preliminary studies on southern pines. Pulp Pap Mag Can 73(12):T400–T404

Knutson I, Lovblad R, Malmström J, De Sousa F, Kringstad KP (1992) Minimizing dioxin formation in mill-scale bleaching of softwood kraft pulp. Tappi J 75(6):112

Kochesfahani SH, Bair C (2002) Overcoming recausticizing limitations; mill experiences with borate autocausticization. In: 7th international conference on new available technologies, Stockholm, Sweden, 4–6 June 2002, pp 87–90

Kochesfahani SH, Bair CM, Kirk M (2006) Partial borate autocausticizing, a new technology in chemical recovery. Appita J 59(2):130–135

Kojima, Y, Yoon, SL (1991) Distribution of lignin in the cell wall of ozonized CTMP fibres. In: Proceedings from the 1991 6th international symposium on wood and pulp chemistry, Melbourne, Australia, p 109

Kojima Y, Yoon SL, Kayama T (1988) A study of production of CTMP from hardwood. Part B : characterization of pulp produced by CTMP-O3 process, Japan Tappi J 42(10): 953–962

Koskinen K (1999) Wood handling applications. In: Gullichsen J, Fogelholm C-J (eds) Papermaking science and technology, Book 6A. Chemical pulping. Fapet Oy, Helsinki, pp 331–491

Ku PWC, Hsieh JS, Jayawant MD, Houle L (1992) Chlorination stage elimination by using nitrosation pretreatment before oxygen delignification/oxygen reinforced extraction. Tappi J 75(10):146–151

Kubes GJ, Fleming BI, Macleod JM, Bolker HI, Werthemann DP (1983) Viscosities of unbleached alkaline pulps.2. The G-factor. J Wood Chem Technol 3(3):313–333

Kuligowski C, Brochier B, Petit-Conil M (2005) New ways to use ozone in bleaching sequences: ozonated water as a last bleaching stage. In: 2005 international pulp bleaching conference, Stockholm, Sweden, 14–16 June 2005, pp 284–287

Kymäläinen M (2001) Fate of nitrogen in the chemical recovery cycle of a kraft pulp mill. PhD thesis, Åbo Akademi University, Turku, Finland

Lachenal D, Papadopoulos J (1988) Improvement of hydrogen peroxide delignification. J Cellul Chem Technol 22(5):537

Lachenal D, Chirat C, Viardin MT (2000) High temperature chorine dioxide delignification. A breakthrough in ECF bleaching of hardwood kraft pulps. Tappi J 83(8):96

Laine J, Stenius P, Carlsson G, Storm G (1996) The effect of ECF and TCF bleaching on the surface chemical composition of kraft pulp as determined by ESCA. Nord Pulp Pap Res J 11(3):201

Lancaster L,Yin C, Renard J, Phillips RB (1992) The effects of alternative pulping and bleaching processes on product performance – economic and environmental concerns. In: Proceedings, EPA international symposium on pollution prevention in the manufacture of pulp and paper. Washington, USA

Larsen E, Kreutz T, Consonni S (1998) Performance and preliminary economics of black liquor gasification combined cycles for a range of kraft pulp mill sizes. In: International chemical recovery conference, vol 2, Tampa, FL, USA, 1–4 June 1998, pp 675–692

Larsen E, Consonni S, Katofsky R (2003) A cost-benefit assessment of biomass gasification power generation in the pulp and paper industry. Final report. Princeton Environmental Institute, October 8, 2003. Princeton University Princeton, NJ, USA

Laubach GD (1998) 1997 TAPPI survey of pulping additives – AQ and chip penetrants, In: TAPPI proceedings: breaking the pulp yield barrier symposium. TAPPI Press, Atlanta, pp 103–111

Lecourt M, Struga B, Delagoutte T, Petit-Conil M (2007) Saving energy by application of ozone in the thermomechanical pulping process. IMPC, Minneapolis, pp 494–507

Lee HL, Yuon HJ, Jung TM (2000) Improvement of linerboard properties by Condebelt drying. TAPPI 83(7)

Lefebvre BE, Santyr GM (1989) Effect of operating variables on kraft recovery boiler performance. Pulp Pap Can 90(12):145–152

Leporini Filho C, Süss HU, Rodrigues da Silva M, Lopes Peixoto MA (2003) Addition of hydrogen peroxide to ozonation for improved bleaching results., ABTCP-TAPPI 2003, 36° Congresso Internacional de Celulose e Papel, São Paulo, Brazil

Levlin JE (1990) On the use of chemi-mechanical pulps in fine papers. Pap Ja Puu-Pap Timber 72(4):301–308

Li J, Gellerstedt G (1997a) On the structural significance of kappa number measurement. In: Preprints 9th international symposium, wood pulping chemistry, vol 1, Montreal, QC, Canada, GI-I

Li J, Gellerstedt G (1997b) The contribution to kappa number from hexenuronic acid groups in pulp xylan. Carbohydr Res 302(3–4):213

Li K, Lei X, Lu L, Camm C (2010) Surface characterization and surface modification of mechanical pulp fibers. Pulp Pap Can 111(1):28–33

Lin B (2008) The basics of foul condensate stripping. Krat recovery short course, Florida, USA

Lindberg H, Engdahl, H, Puumalinen R (1994) Strategies for metal removal control in closed cycle mills. In: 1994 proceedings of the international pulp bleaching conference. CPPA, Montreal

Lindblom M (2006) Chemrec pressurized black liquor gasification – status and future plans. In: 7th international colloquium on black liquor combustion and gasification, Jyväskylä, Finland, 31 July – 2 August 2006

Lindgren CT, Lindström ME (1996) The kinetics of residual delignification and factors affecting the amount of residual lignin during kraft pulping. J Pulp Pap Sci 22(8):J290–J295

Lindholm CA (1977a) Ozone treatment of mechanical pulp. Part 2: influence on strength properties, Pap Ja Puu 59(2):47–50, 53–58, 60, 62

Lindholm CA (1977b) Ozone treatment of mechanical pulp. Part 3: influence on optical properties, Pap Ja Puu 59(4a):217–218, 221–224, 227–232

Lindholm CA (1977c) Ozone treatment of mechanical pulps. Pap Ja Puu (Special No. 4a):217–231.

Lindholm CA, Gummerus M (1983) Comparison of alkaline sulphite and ozone treatment of SGW, PGW and TMP fibre's. Pap Ja Puu 65(8):467–473

Lindstrom LA (2003) Impact on bleachability and pulp properties by environmentally friendly bleaching concepts. In: Metso paper pulping technology seminar, Hyderabad, India, November 2003

Lindström LÅ, Larsson, PE (2003) Fiber lines for bleached eucalyptus kraft pulps. Impact on bleachability and paper properties. In: Conference in Vicosa, Brasil, 4–5 September 2003

Lindström ME, Teder A (1995) The effect of polysulfide pretreatment when kraft pulping to very low kappa numbers. Nord Pulp Pap Res J 10(1):8

Lindstrom LA, Norden S, Wennerstrom M (2007) High consistency ozone bleaching: present status and future. IPPTA 19(1):83–86

Lönnberg B (2009) Papermaking science and technology, Book 5, mechanical pulping, Chapter 7, Thermomechanical Pulping, pp 214–221, Paperi ja Puu Oy

Löwendahl L, Samuelsson O (1978) Carbohydrate stabilization during soda pulping with addition of antraquinone. Tappi 61(17):566

Lyon RK (1979) Thermal DeNOx: How it works. In: Hydrocarbon processing, October. Gulf Publishing Co., Houston, Texas

Lyon RK (1987) Thermal DeNO: controlling nitrogen oxides emissions by a noncatalytic process, Environ Sci Technol 21(3):231

Magara K, Ikeda I, Tomimura Y, Hosoya S (1998) Accelerated degradation of cellulose in the presence of lignin during ozone bleaching. J Pulp Pap Sci 24(8):264

Magnotta V, Kirkman A, Jameel H, Gratzl J (1998) High kappa pulping and extended oxygen delignification to increase yield, Breaking the pulp yield barrier symposium, Atlanta, February 17–18 1998, Tappi Press, Atlanta, pp 165–182

Mahmoudi S, Baeyens J, Seville JPK (2010) NOx formation and selective non-catalytic reduction (SNCR) in a fluidized bed combustor of biomass. Biomass Bioenergy 34:1393–1409

Mäkinen T, Alakangas E, Kauppi M (2011) BioRefinery yearbook 2011. Tekes, Helsinki

Maleshenko A, Ilmoniemi E, Kaasalainen H (2008) Web-forming unit of a paper or board machine. WO 2006120294 (A1)

Malinen R, Rantanen T, Rautonen R, Toikkanen L (1994) TCF bleaching to high brightness – bleaching sequences and pulp properties. In: Paper presented at 1994 international pulp bleaching conference held at Vancouver, Canada, 13–16 June 1994, Paper presentations, pp 187–194

Malkov Y (1990) A polysulfide liquor regeneration process with the use of an MT catalyst. Pap Ja Puu 72(10):961–966

Malmström J (2010) NOx emissions from Swedish recovery boilers. Swedish Forest Industries Federation, Sweden

Mansour MN, Steedman, WG, Durai-Swamy K, Kazares, RE, Raman TV (1992) Chemical and energy recovery from black liquor by steam reforming. In: International chemical recovery conference, Seattle, WA, USA, 7–11 June 1992

Mansour MN, Durai-Swamy K, Aghamohammadi B (1993). Pulsed combustion process for black liquor gasification. Second annual report U.S. DOE report DOE/CE/40893-T2 (DE94002668)

Mansour MN, Durai-Swamy K, Warren DW (1997) Endothermic spent liquor recovery process, U.S. Patent no 5,637, 192

Mao X, Kim J, Tran H, Kochesfahani SH (2006) Effect of chloride and potassium on borate autocausticizing reactions during black liquor combustion, Pulp Pap Can 107(10):T201–T204

Maples GM, Ambady R, Caron JR, Stratton SC, Vega Canovas RE (1994) BFR™: a new process toward bleach plant closure. Tappi J 77(11)

Marechal AJ (1993) Acid extraction of alkaline wood pulps before or during bleaching: reason and opportunity, Wood Chem Technol 13(2):261

Martin N, Anglani N, Einstein D, Khrushch M, Worrell E, Price L (2000a) Opportunities to improve energy efficiency and reduce greenhouse gas emissions in the U.S. Pulp and Paper Industry. Lawrence Berkeley National Laboratory, LBNL-46141, Berkeley

Martin N, Worrell E, Ruth M, Price L, Elliott RN, Shipley AM, Thorne J (2000b) Emerging energy-efficient industrial technologies. Lawrence Berkeley National Laboratory, LBNL-46990, Berkeley

Martius C (1992) Density, humidity, and nitrogen content of dominant wood species of floodplain forests (várzea) in Amazonia. Holz Roh Werkst 50:300–303

McCubbin N (1996) Numerous recovery options offer solutions for mill effluent closure. Pulp Pap Mag March 1996. Available online. www.risiinfo.com/db_area/archive/p_p_mag/1996/9603/96030131.htm

McCubbin N (2001a) Spill control: assessing your situation. Solutions 84(11):49–50

McCubbin N (2001b) Spill control. Part II: Reducing spills. Solutions 84(12):36–37

McDonough TJ (1990) Oxygen delignification. In: Tappi bleach plant operations short course, Hilton Head, Tappi press

McDonough TJ (1995) Recent advances in bleached chemical pulp manufacturing technology. Tappi J 78:55–62

McDonough TJ (1996) Oxygen delignification. In: Dence CW, Reeve DW (eds) Pulp bleaching – principles and practice. Tappi Press, Atlanta, p 213

McDonough T, Herro J (1997) Influence of low-lignin pulping conditions on bleachability; effects of anthraquinone and effective alkali charge, anthraquinone pulping: TAPPI Press Anthology of Published Papers 1977–1996 (Goyal G. ed.) Chapter 1, pp 129–133

McGowan D R (2002) White water reuse in high-pressure paper machine showers. Preprints 88th PAPTAC annual meeting, Montreal, QC, Canada, 29–31 January 2002 [Pulp and Paper Technical Association of Canada, Montreal, Canada: 2002), pp B125–B128

Mckeough P (2003) Evaluation of potential improvements to BLG technology. Colloquium of black liquor combustion and gasification. Utah, Park City, 12 p

Mehra NK (1979) Recausticizing and lime mud reburning, Tappi 62(9):47–51

Meller A (1963) Retention of polysaccharides in kraft pulping. Part 1. The effect of borohydride treatment of Pinus radiata wood on its alkali stability. Tappi 46(5):317–319

Meller A, Ritman BL (1964) Retention of polysaccharides in kraft pulping. Part II. The effect of borohydride addition to kraft liquor on pulp yield, chemical characteristics and papermaking properties of Pinus radiata pulps. Tappi 47(1):55–64

Michniewicz M, Janiqa M (2010) The technique for sodium carbonate autocausticization with sodium metaborate. Polish Pap Rev 66(5):263–268

Middleton T (2006) Steam reforming technology at the norampac trenton mil. Presentation at IEA meeting, annex XV black liquor gasification, Washington, DC, USA, 20–22 February 2006.

Moldenius S (1995) Pulp quality and economics of ECF vs. TCF. In: Presentation, international non-chlorine bleaching conference. Amelia Island, Florida

Moldenius S (1997) Mill experience with ECF and TCF bleaching facts vs. fiction. In: Proceedings of the international emerging technologies conference, Orlando, FL

Mutton DB (1958) Hardwood resin. Tappi 41(11):632–643

Naqvi M, Yan J, Dahlquist E (2010) Black liquor gasification integrated in pulp and paper mills: a critical review. Bioresour Technol 101:8001–8015

Naqvi M, Yan J, Dahlquist E (2012) Bio-refinery system in a pulp mill for methanol production with comparison of pressurized black liquor gasification and dry gasification using direct causticization. Appl Energy 90(1):24–31

National Council for Air and Stream Improvement (NCASI) (2012) Pulp and paper mill emissions of SO_2, NOx, and particulate matter in 2010. Special report no. 12–03. National Council for Air and Stream Improvement Inc, Research Triangle Park

National Council for Air and Stream Improvement (NCASI) (2013) Overview of effects of decreased SOx and NOx emissions. www.paperenvironment.org/PDF/SOxNOx/SOxNOx

Nelson PJ (1998) Elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching of pulps. In: Young RA, Akhtar M (eds) Environmentally friendly technologies for the pulp and paper industry. Wiley, New York, p 215

Nesaratnam S (1998) Effluent treatment. Pira environment guide series, Pira International, Leatherhead, p 72

Newport DG, Rockvam 1, Rowbotton R (2004) Black liquor steam reformer start-up at Norainpac. In: Proceedings of TAPPI international chemical recovery conference, South Carolina

Ni Y, Kubes GJ, van Heiningen ARP (1992) Rate processes of chlorine dioxide distribution during prebleaching of kraft pulp. Nord Pulp Pap Res J 7(4):200–204

Nichols KM, Thompson, LM, Empie HJ (1993) A review of NOx formation mechanisms in recovery furnaces. Tappi J 76(1):119–124

Niiranen M (1985) Study of debarking drum process dimensioning. Doctoral thesis. Helsinki University of Technology

Nilsson J (1998) A literature survey of impulse drying, 1994–1998. Technical report. LUTKDH/(TKKA-7004)/1-36/1998. Lund University

Nilsson LJ, Larson ED, Gilbreath KR, Gupta A (1995) Energy efficiency and the pulp and paper industry. ACEEE, Washington, DC/Berkeley

Nilsson P, Puurunen K, Vasara P,Jouttijarvi T (2007) Continuum – rethinking BAT emissions of the pulp and paper industry in the European Union, Finnish environment report 12/2007. 41 pp

Nordén S, Teder A (1979) Modified kraft processes for softwood bleached-grade pulp. Tappi 62(7):49–51

Nordic Council of Ministers (1993) Study on nordic pulp and paper industry and the environment. Nordic Council of Ministers, Copenhagen

Northeast States for Coordinated Air Use Management (NESCAUM) (2005) Assessment of control options for BART-eligible sources. Steam electric boilers, industrial boilers, cement plants and paper and pulp facilities. Northeast States for Coordinated Air Use Management In Partnership with The Mid-Atlantic/Northeast Visibility Union. www.nescaum.org/documents/bart-controlassessment.pdf/

Norvall G, Burton T, Kanters C (2001) The removal of pulp mill odors by novel catalytic environmental technology. Pulp Pap Can 102(4):T111–T113

Nurmesniemi H (2010) Tertiary treatment of biologically treated waste water from the pulp and paper mill – internal report assessing findings of the WWF report on the Celco pulp mill in Valdivia, Chile, Sora Enso Oyj, Environmental affairs, 2010, p 2

Nutt WE, Griggs BF, Eachus SW, Pikulin MA (1993) Developing an ozone bleaching process. Tappi J 76(3):115–213

Obst JR, Landucci LL, Sanyer N (1979) Quinons in alkaline pulping. Tappi 62:1, 55

Oinonen H (2010) Ozone bleached pulp and fine papers. Results Pulp Pap (2):35–38

Ojala T (1999) Condebelt drying process benefiting paper- and boardmanufacturing and converting. In: Presentation at Aticelca/ATI Convention in Milan, April 19, 1999, Energetic evolution in the paper sector

Pan GX (2001) An insight into the behaviour of aspen CTMP in peroxide bleaching – alkalinity's influence is greater than that of peroxide charge. Pulp Pap Can 102(11):41–45

Panchapakeshan B, Hickman E (1997) Fiberline advancements spur papermaking process changes. In: Patrick KL (ed) Advances in bleaching technology. Miller Freeman Books, San Francisco, p 82

PARCOM (1994) BAT and BEP for the Sulphite and Kraft Pulp Industry, PARCOM, ISBN 0946 56 367

Parker ET, Lundsted LG (1975) U.S.A. Patent 3,909,345

Parthasarathy VR (1997) Oxidative extraction of hardwood and softwood kraft pulps with sodium carbonate-sodium hydroxide mixtures or oxidized white liquor during multistage bleaching. Tappi J 80(10):253–261

Parthasarathy VR, Rudie GF, Detty AE (1993) Total chlorine dioxide substitution in short sequence bleaching and it's effect on pulp brightness and effluent characteristics. In: Tappi pulping conference proceedings. Tappi Press, Atlanta, p 933

Pekkala O (1982) On the extended delignification using polysulfide or anthraquinone in kraft pulping. Pap Ja Puu 64(11):735–744

Pekkala O (1986) Prolonged kraft cooking modified by anthraquinone and polysulfide. Pap Ja Puu 68(5):385–400

Pereira ER, Colodette JL, Barna J (1995) Peroxide bleaching in pressurised equipment: influence of temperature and consistency. Papel 56(12):61–67

Persson H (1994) A literature review of impulse drying, 1988–1994. Technical report LUTKDH/(TKKA-7005)/1-42/1994. Lund University

Peter W (1993) First experience with mill-scale ozone bleaching, non-chlorine bleaching conference, Miller Freeman, San Francisco, CA, USA, 1993, Paper 22

Petit-Conil, M (1995) Principes de préparation des pâtes CTMP de bois résineux et feuillus. Application à la mise au point de procédés, Thèse de l'Institut National Polytechnique de Grenoble

Petit-Conil M (2003) Use of ozone in mechanical pulping processes. ATIP 57(2):17–26

Petit-Conil M, de Choudens C (1994) A new chemithermomechanical process : use of oxygen in the primary refining stage. Part 1: oxidative sulfonation for hardwood and softwood CTMP pulping. Das Pap 48(10):628–634

Petit-Conil M, Robert A, Pierrard JM (1997) Fundamental principles of mechanical pulping from softwoods and hardwoods. Part 1: theoretical aspects. Cellul Chem Technol 31(1/2):93–104

Petit-Conil M, de Choudens C, Espilit T (1998) Ozone in the production of softwood and hardwood high-yield pulps to save energy and improve quality. Nord Pulp Pap Res J 13(1):16–22

Pettersson SE, Rydholm SA (1961) Hemicelluloses and paper properties of birch pulps, Part 3. Sven Pap 64(1):4–17

Pikka O, Vessala R, Vilpponen A, Dahllof H, Germgard U, Norden S, Bokstrom M, Steffes F, Gullichsen J (2000) Bleaching applications. In: Gullichsen J, Fogelholm C-J (eds) Chemical pulping –papermaking science and technology. Fapet Oy, Helsinki, Finland, Book 6A, p A19

Pipon G, Chirat C, Lachenal D (2005) Final bleaching with ozone – basic and applied aspects. IPBC, Stockholm, pp 138–143

Pöyry J (1992) Reduction of atmospheric emissions from pulp industry, on behalf of Swedish EPA

Pöyry J (1997) A compilation of BAT techniques in Pulp and Paper Industry. Jaakko Pöyry Oyj, 1997, Finland

Prakash CB, Murray FE (1973). Studies on H2S emission during calcining, Pulp Pap Mag Can 74(5):99–102

Program SNB (2011) Gasification of black liquor, popolar scientific summary of the BLG II – program 2007–2010. Retrieved on March 15, 2012. Available at: http://www.etcpitea.se/pdf/BLG_eng.pdf

Pryke DC (1997) Elemental Chlorine-Free (ECF): pollution prevention for the pulp and paper industry. http://www.ecfpaper.org/science/science.html (April 1997)

Pryke DC (2003) ECF is on a roll: it dominates world bleached pulp production. Pulp Pap Int 45(8):27–29

Pryke DC, Farley B, Wolf A (1995) Implementation of ECF bleaching at Mead Paper Co., Chillicothe, Ohio. In: Tappi pulping conference proceedings. TAPPI PRESS, Atlanta

Quinde A (1994) Pulping additives in kraft pulping: past, present and future. In: 1994 Spring conference, Canadian Pulp and Paper Association. Jasper, Alberta. May 19–2

Quinde A, Brogdon, B, Fowler L, Lee C (2004) A decade of AQ benefits at Canfor's Northwood Mill (1994–2004). In: 2004 TAPPI Fall technical conference. Atlanta, GA, USA, October 31–November 3, 2004

Radojevic M (1998) Reduction of nitrogen oxides in flue gases. Environ Pollut 102:685–689

Ragauskas AJ, Poll KM, Cesternino AJ (1993) Effect of xylanase pretreatment procedures for non-chlorine bleaching. IPST technical paper series, no. 482, Institute of Paper Science, Atlanta, 1993

Ragnar M (2002) Modification of the D0 stage into D* makes 2-stage bleach plant for HW kraft pulp a reality. TAPPI international pulp bleaching conference. Portland, OR. Tappi Press, Atlanta

Ragnar M, Dahllöf H (2002) Kvaerner pulping, ECF bleaching of eucalypt kraft pulp bleaching chemical needs and yellowing characteristics of different sequences. Nord Pulp Pap Res J 17:3, 228–233

Rajotte A (2000) Technology and environmental policy: case study on chlorine policies in the P&P sector in Finland, France, and Sweden, School of Business and Economics, University of Jyväskylä, Finland. In: 4th framework programme of DG XII of the European Commission, Contract ENV4-CT97-0604, 2000.

Rampotas C, Terelius H, Jansson K (1996) The netfloc system – the tool to remove extractives and NPE. In: Proceedings of the 1996 minimum effluent mills symposium, Atlanta

Rapson WH, Anderson CB (1978) Kraft pulp bleaching with chlorine and chlorine dioxide. Tappi J 61(10):97

Ratnieks E, Ventura JW, Mensch MR, Zanchin RA (2001) Acid stage improves production in eucalyptus fibreline. P&P Can 102:12

Reeve DW (1996) In: Dence CW, Reeve DW (eds) Pulp bleaching – principles and practice. Tappi Press, Atlanta, pp 263–287

REHVA (2005) Electrostatic precipitators for industrial applications. REHVA guidebook, REHVA – Federation of European Heating and Air-conditioning Assosiations. REHVA, Brussels, p 117

Reis R (2001) The increased use of hardwood high yield pulps for functional advantages in paper-making. In: Proceedings of the 2001 papermakers conference, Cincinnati, OH, USA, pp 87–108

Rentz O, Schleef, HJ, Dorn R, Sasse H, Karl U (1996) Emission control at stationary sources in the Federal Republic of Germany, Volume I, Sulphur oxide and Nitrogen oxide emission control, French-German Institute for Environmental Research University of Karlsruhe (TH), Karlsruhe, August 1996

Retulainen E (2001) Key development phases of condebelt: long journey from idea to commercial product. Dry Technol 19(10):2451–2467

Retulainen E, Hamalainen A (2000) Three years of condebelt drying at stora enso's pankakoski mill. TAPPI 83(5):1–8

Retulainen E, Merisalo N, Lehtinen J, Paulapuro H (1998) Effect of condebelt press drying in sheet structure and properties. Pulp Pap Can 99(1):53–58

Rice RC, Netzer A (1982) Handbook of ozone technology and applications. Ann Arbor Science, Ann Arbor

Robert DR, Szadeczki M, Lachenal D (1999) Chemical characteristics of lignins extracted from softwood TMP after O_3 and ClO_2 treatment. In: Proceedings from the 215th national ACS meeting, Lignin: historical, biological and materials perspectives, Dallas, Texas, USA, chapter 27, pp 520–531

Rockvam LN (2001) Black liquor steam reforming and recovery commercialization. In: International chemical recovery conference, Whistler, Canada, 11–14 June 2001

Rodrigues da Silva M, Peixoto MAL, Colodette JL (2002) Mill experience using a hot acid stage for eucalyptus kraft pulp bleaching. In: TAPPI international pulp bleaching conference. Portland, OR. Tappi Press, Atlanta

Rothenberg S, Shaw J, Durst WB (1981) Effect of chemical modification on the properties of lignin-containing fibres. Pap Ja Puu 63(3):111–114, 117–119

Roy-Arcand L, Archibald F (1996) Selective removal of resin and fatty acids from mechanical pulp effluents by ozone. Water Res 30(5):1269–1279

RPDC (2004) Development of new environmental emission limit guidelines for any new bleached eucalypt Kraft pulp mill in Tasmania- volume 1. Resource Planning and Development Commission, Tasmania

Ruffini G (1966) Improvement of bonding in wood pulps by the presence of acidic groups, Svensk Papperstding 69(3):72

Ryham R, Nikkanen S (1992) Liquor heat treatment and its impact on chemical recovery. In: Proceedings of the 1992 European pulp & paper week, Bologna, Italy, May 1992

Sabourin M (2007) Minimizing TMP energy consumption using a combination of chip pre-treatment, RTS and multiple stage low consistency refining. In: 25th international mechanical pulping conference, Minneapolis, MN, USA, May 6–9, Tappi, Atlanta, GA, USA, 8 pp

Sabourin MJ, Hart PW (2010) Enhanced fiber quality of black spruce (Picea mariana) thermomechanical pulp fiber through selective enzyme application. Ind Eng Chem Res 49:5945–5951

Sabourin M, Aichinger J, Wiseman N (2003) Effect of increasing wood chip defibration on thermomechanical and chemi-thermomechanical refining efficiency, In: International mechanical pulping conference, Quebec City, pp 163–170

Saharinen E, Nurminen I (2001) Improving internal bonding strength and bulk for folding boxboard middle layer by ozone treatment. In: Proceedings from the 2001 international mechanical pulping conference, Helsinki, Finland, pp 119–124

Salo M (1999) Environmental best practices in the forest cluster, Interim Report IR-00-015, International Institute for Applied Systems Analysis, Vienna, Austria

Santos RE, Backlund JC (1992) Firing of non-condensible waste gas streams in stand alone modular incineration systems. In: Presented at the 1992 incineration conference, Albuquerque, New Mexico, Session XXI

Scheriau R (1972) Theorie der trommelentrindung unter besonderen berücksichtigung der trockenentrindung . Dissertation an der Technischen Hochschule Graz

Schroderus S, Carter D, Brumme H (2000) Upgrade of lime kiln and causticizing plant in kraft mill. Pulp Pap Can 101(1):74–78

Sebbas E (1988) Reuse of Kraft Mill secondary condensates. Tappi J 71(7):53–58

SEPA-Report 4712-4 (1997a) Energy conservation in the pulp and paper industry. Jaakko Pöyry Consulting AB, Scotland, 1997

SEPA-Report 4713-2 (1997b) Aspects on energy and environment costs in connection with production of kraft pulp, Recycled fibre and TMP. Jaakko Pöyry Consulting AB, Scotland, 1997

Sezgi US, Kirkman AG, Jameel H, Chang H, Morrison JJ, Bianchini CA, Wilson JRA (1994) Combined discrete-continuous simulation model of an RDH tank farm. Tappi J 77(7):213–220

Sharma KD (2010) ITC's experience with light ECF bleaching (ozone). IPPTA 22(1):131–133

Sheats A (2010) Ozone bleaching: environmental, production, and cost benefits. Pap Asia 26(3):24–26, 28

Shrinath SA, Bowen I.J (1993) An overview of AOX regulations and reduction strategies, In: Tappi pulping conference proceedings, Atlanta 14–18.11.1993, pp 1–15

Siltala M, Winberg K (1999) The use of bleach plant filtrate for post-oxygen washing: a way to save money and the environment. In: Proceedings of the 27th EUCEPA conference – crossing the millennium frontier, emerging technical and scientific challenges, Grenoble, France, pp 11–14

Simons HA, AF-IPK (1992) Multi-client study. In: Towards kraft mill 2000, Vancouver, Canada, Book 2, p 54

Sjöblom K, Mjöberg J, Hartler N (1983) Extended delignification in kraft cooking through improved selectivity .1. The effects of the inorganic composition of the cooking liquor. Pap Puu 65(4):227–240

Sjödahl RG, Axelsson P, Lindström ME (2006) Addition of dissolved wood components to improve the delignification rate and pulp yield in hardwood kraft pulping. Appita J 59(4):317–320

Smook GA (1992) Handbook for pulp & paper technologists, 2nd edn. Angus Wilde Publications, Vancouver, p 36

Soteland N (1977) The effect of ozone on mechanical pulps, Pulp Pap Can 78(7):45–48

Soteland N (1982) Interstage ozone treatment of hardwood high yield pulp. Pap Ja Puu 64(11):707–708, 710, 712–714

Soteland N, Loras V (1974) The effect of ozone on mechanical pulps. Norsk Skogind 28(6):165–169

Springer EL (1997) Delignification of wood and kraft pulp with peroxomonophosphoric acid. J Pulp Pap Sci 23(12):582

Sricharoenchaikul V (2001) Fate of carbon-containing compounds from gasification of kraft black liquor with subsequent catalytic conditioning of condensable organics. Ph.D dissertation, Georgia Institute of Technology, 2001

Steen B, Stijnen T (1984) Hydrogen sulfide formation in a lime kiln at a kraft mill, Svensk Papperstidning 87(3):R14–R17

Steffes F, Germgard U (1995) ECF, TCF upgrade choices key on world market, environmental forces. Pulp Pap 69(6):83–92

Stenström S (1989) Impulstorkning av papper. STU projekt 742-88-02837. Lunds Tekniska Högskolan, (in Swedish)

Stigsson L (1998) Chemrec black liquor gasification. In: International chemical recovery conference, Tampa, Florida, USA, 1–4 June 1998

Stitt, EH, Fakley ME (1995) New process for the abatement of odors and low level VOCs. preprints. AIChE Spring meeting, Houston, TX, March, 1995

Strakes G, Bielgus J (1992) New chip thickness screening system boosts efficiency, extends wear life. Pulp Pap, July, p 93

Stratton S, Gleadow P (2003) Pulp mill process closure: a review of global technology developments and mill experiences in the 1990s. Technical bulletin no. 860. Research. National Council for Air and Stream Improvement, Inc., Triangle Park

Stratton S, Gleadow P, Johnson A (2003) Pulp mill process closure: a review of global technology developments and mill experiences. In: The 1990s international Water Association conference, Seattle, USA

Stubenvoll J, Holzerbauer, E, Böhmer, S (2007) Overview of NOx and dust emissions of the Austrian pulp and paper industry, Unweltbundesamt, 2007

Suhr M (2000) The BREF in the pulp and paper industry. BAT for an industry with a large variety of raw materials and products. In: European conference on the seville process: a driver for environmental performance in industry, April, 6–7, Stuttgart, Germany

Sun, Y, Lanouette R, Pelletier E, Cloutier JN, Epiney M (2013) Impact of pH during an interstage ozone treatment of thermomechanical pulp. In: PACWEST conference, Kamloops, BC, Canada, 6 pages

Sun Y, Lanouette R, Pelletier E, Cloutier JN, Epiney M (2014a) Fibre performance of mechanical pulp after selective refining combined with interstage ozone treatment. In: IMPC conference, Helsinki, Finland, 10 pages

Sun Y, Lanouette R, Cloutier JN, Pelletier E, Épiney M (2014b) Impact of selective refining combined with inter-stage ozone treatment on thermomechanical pulp. BioResources 9(1):1225–1235

Süss HU, Del Grosso M (2002) Bleaching of eucalyptus kraft pulp to market pulp brightness in only 2 stages. In: Appita Conference, Rotorua, New Zealand

Suss HU, Schmidt K, Del Grosso M, Mahagaonkar M (2000) Peroxide application in ECF sequences: a description of the state-of-the-art. Appita 53(2):116–121

Talja R, Bäckström, M, Kilian M (1998) Impulse technology – a paper making process for tomorrow, EcoPaperTech, 1998. KCL, Helsinki

Tamminen T, Forssen M, Hupa M (2002) Dust and flue gas chemistry during rapid changes in the operation of black liquor recovery boilers: Part 3 – gaseous emissions. Tappi J 1(7):25–29

Tana J, Lehtinen KJ (1996) The aquatic environmental impact of pulping and bleaching operations – an overview. Finnish Environmental Agency, Helsinki

Tatsuishi H, Hatano T, Iwai T, Kovasin K (1987) Practical experiences of medium consistency oxygen delignification by Rauma-Repola and Sumitomo heavy industries. In: Tappi international oxygen delignification conference proceedings. Tappi Press, Atlanta, p 209

Teder A (1968) Redox potential of polysulphide solutions and carbohydrate stabilisations. Sven Pap 71(5):149

Teder A, Olm L (1981) Extended delignification by combination of modified kraft pulping and oxygen bleaching. Pap Puu 63(4a):315–326

Teixeira DP, Muzio LJ, Montgomery TA (1991) Effect of trace combustion species on SNCR performance. In: International conference on environmental control of combustion processes, joint meeting of the American Flame Research Committee and the Japanese Flame Research Committee, Honolulu, HI. October, 1991

Telkkinen, UT (1997) Typen määrä ja vaikutukset sulfaattisellutehtaan kemikaalikierrossa johdettaessa valkaisun vedet kemikaalien talteenottoon. Lic. Tech. thesis. Helsinki University of Technology, Espoo, Finland. (in Finnish)

Tench L, Harper S (1987) Oxygen bleaching practices and benefits – an overview. In: Tappi international oxygen delignification conference proceedings. Tappi Press, Atlanta, p 1

Tenkanen M, Gellerstedt G, Vuorinen T, Teleman A, Perttula M, Li J, Buchert J (1999) Determination of hexenuronic acid in softwood kraft pulps by three different methods. J Pulp Pap Sci 25(9):306

Tervola P, Gullichsen J (2007) Confidence limits in mass balances with application to calculation of pulp washing efficiency. Appita J 60(6):474–481

Theodore L (2008) Electrostatic precipitators in air pollution control equipment calculations, Wiley, 2008

Thornton J, Ekman R, Holmbom B, Eckerman C (1993) Release of potential anionic trash in peroxide bleaching of mechanical pulp. Pap Ja Puu-Pap Timber 75(6):426–431

Tikka PO, Tahkenen H, Korasin KK (1992) Chip thickness vs. kraft pulping performance, Part I: experiments by multiple hanging baskets. In: Proceedings, 1992 Tappi pulping conference, Boston MA, November 1992, p 555

Tran HN, Barham D (1991) An overview of ring formation in lime kilns. Tappi J 74(1):131–136

Tran HN, Mao X, Barham D (1993) Mechanisms of ring formation in lime kilns, J Pulp Pap Sci 19(4):167–174

Tran H, Bair CM, McBroom RB, Strang W, Morgan B (2001) Partial autocausticizing of kraft smelt with sodium borates. Tappi/Solutions! 84(9):1–16

Tran KQ, Kilpinen P, Kuma N (2008) In-situ catalytic abatement of NOx during fluidized bed combustionda literature study. Appl Catal B Environ 78:129–138

Troughton N, Sarot P (1992) The efficient use of hydrogen peroxide as a chemical pulp delignification agent: the macrox system. In: Proceedings Tappi pulping conference. TAPPI PRESS, Atlanta, GA, USA, p 519

Tucker P (2002) Changing the balance of power. Solutions 85(2):34–38

Tutus A (2005) The utilization of the boron compounds in pulping and bleaching. In: National boron symposium proceedings, Ankara, 2005, pp 399–404

Tutus A, Usta M (2004) Bleaching of chemithermomechanical pulp (CTMP) using environmentally friendly chemicals. J Environ Biol 25:141–145

Ulmgren P, Rådeström R (1997) The build-up of phosphorus in a kraft pulp mill and the precipitation of calcium phosphate from green and white liquors. J Pulp Pap Sci 23(2):J52–J58

United Nations Environment Programme (UNEP) (2006) Draft guidelines on best available techniques and provisional guidance on best environmental practices relevant to Article 5 and Annex C of the Stockholm convention on persistent organic pollutants, revised working draft version 25 April 2006 www.chem.unep.ch/pops/

Urbanski R, Lister S, Raoul D (1998) Development of an effective TRS and odor reduction program. Pulp Pap Can 99(8):T278–T281

USEPA (1992) Model pollution prevention plan for the kraft segment of the pulp and paper industry. Region 10, Seattle, WA. EPA 910/9-92-030, September, 1992

USEPA (1976) Technology transfer, environmental pollution control, pulp and paper industry, Part 1: Air, EPA 625/7-76-001.

USEPA (1997) Supplemental technical development document for effluent limitations guidelines and standards for the pulp and paperboard category – subpart B and subpart E. U.S. Environmental Protection Agency, Washington, DC, USA, October 1997. Available online at http://water.epa.gov/scitech/wastetech/guide/pulppaper/upload/1997_12_12_guide_pulppaper_jd_stdd-v4.pdf

USEPA (1998a) Federal register notices for final air and water rules, (63 FR 18504–18751, April 15, 1998 and 63 FR 42238–42240, August 7, 1998) www.epa.gov/OST/pulppaper/cluster.html

USEPA (1998b) Pulp and paper NESHAP: a plain English description www.epa.gov/ttnatw01/pulp/guidance.pdf

USEPA (2007) Fact sheet – final amendments to the regional haze rule and guidelines for Best Available Retrofit Technology (BART) determinations. United States Environmental Protection Agency, Washington, DC. http://www.epa.gov/visibility/fs_2005_6_15.html

USEPA (2011) Sulfur dioxide designations and EPA response. United States Environmental Protection Agency, Washington, DC. http://www.epa.gov/air/sulfurdioxide/designations/state.htm

Vakkilainen EK, Kankkonen S, Suutela J (2008) Advanced efficiency options: increasing electricity generating potential from pulp mills. Pulp Pap Can 109(4):14–18

Van heiningen A, Ji Y (2012) Southern pine oxygen delignified pulps produced in a Berty throughflow reactor: how to obtain the highest degree of delignification while maintaining pulp yield and quality. Tappi J 11(3):9–17

Van Jiang Z-H, Lierop B, Berry R (2000) Hexenuronic acid groups in pulping and bleaching chemistry. TAPPI J 83:1

Van Lierop B, Skothos A, Liebergott N (1996) Section IV: the technology of pulp bleaching, Chapter 5: ozone delignification. In: Dence CW, Reeve DW (eds) Pulp bleaching principles and practices. Tappi Press. Atlanta

Vasara P, Jappinen H, Lobbas P (2001) A strategic concepts for best available techniques in the forest industry. Finnish Environment Institute, Oy Edita Ab, Helsinki, p 73.

Vasudevan B, Panchapakesan B, Gratzl, JS, Holmbom B (1987) The effect of ozone on strength development and brightness reversion characteristics of high yield pulps. In: Proceedings from the 1987 Tappi pulping conference, proceedings, Washington, DC, pp 517–523

Vehmaa J, Pikka O (2007) Proceedings of the paperex 2007, New Delhi, India

Verveka P, Nichols KM, Horton RR, Adams TN (1993) The form of nitrogen in wood and its fate during kraft pulping. In: Proceedings of the Tappi 1993 environmental conference, Tappi Press, Atlanta, pp 777–780

Vuorinen T, Taleman A, Fagerstrom P, Buchert J, Tenkanen M (1996) Selective hydrolysis of hexenuronic acid gr oups and its application in ECF and TCF bleaching of kraft pulps. In: International pulping bleaching conference, Washington DC, USA, Book 1, p 43

Vuorinen T, Fagerstrom P, Rasanen E, Vikkula A, Henrisson K, Teleman A (1997) Selective hydrolysis of hexenuronic acid groups opens new possibilities for development of bleaching processes. In: 9th international symposium on wood and pulping chemistry, Montreal, QC, Canada, p M4-1

Vuorinen T, Fagerstrom P, Buchert J, Tenkanen M, Teleman A (1999) Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps. JPPS 25:5

Wahren D (1978) Förfarande och anordning för konsolidering och torkning av en fuktig porös bana. Swedish patent no. 7803672-0

Walkush K, Gustafson RR (2002) Application of pulping models to investigate the. Performance of commercial continuous digesters. Tappi J 1(5):13–19

Walsh PB, Secombe RC, Hoyos M (1991) Practical mill experience with the use of hydrogen peroxide reinforced extraction stages to reduce and/or eliminate the use of elemental chlorine in hardwood kraft Pulps for AOX reduction. In: Paper presented at pulping Conference held 3–7 November at Orlando, FL, USA: Book 1, p 35

Walter JC (1996) Water reuse through filtration. In: Proceedings of the 1996 Tappi engineering conference (Electronic, available at Tappi website). TAPPI, Atlanta, GA

Wang L, Templer R, Murphy RJ (2012) High-solids loading enzymatic hydrolysis of waste papers for biofuel production. Appl Energy 99:23–31

Wannenmacher PN, Frederick WJ, Hendrickson KA, Holman KL (1998) The solubility of aluminosilicates in kraft green and white liquors. In: Proceedings of the 1998 international chemical recovery conference. Tappi Press, Atlanta

Warnqvist B, Delin L, Theliander H, Nohlgren I (2000) Teknisk ekonomisk utvärdering avsvartlut-förgasningsprocesser. Värmeforsk Service AB, Stockholm

Wedin H (2012) Aspects of extended impregnation kraft cooking for high-yield pulping of hardwood. Ph.D thesis, KTH Royal Institute of Technology, Stockholm, Sweden

Wennerström M (2002) Decreasing brightness reversion with powerful ozone bleaching, at IPBC, Portland, Oregon, USA, p 265

Whitty K, Baxter L (2001) State of the art in black liquor gasification technology. In: Joint international combustion symposium, Kauai, Hawaii, 9–12 September 2001

Whitty K, Nilsson A (2001) Experience from a high temperature, pressurized black liquor gasification pilot plant. In: International chemical recovery conference, Whistler, Canada, 11–14 June 2001

Whitty K, Verrill CL (2004) A historical look at the development of alternative black liquor recovery technologies and the evolution of black liquor gasifier designs. In: International chemical recovery conference, Charleston, SC, USA, 6–10 June 2004

Wilson J (1993) Results from improved brown stock washing. In: TAPPI pulping conference, proceedings. Atlanta, GA, USA, pp 155–157

Woodman J (1993) Pollution prevention technologies for the bleached kraft segment of the U.S pulp and paper industry. US EPA, Washington, DC

World Bank (1998) Nitrogen oxides: pollution prevention and control pollution prevention and abatement handbook. World Bank Group, Washington, DC, pp 245–249

Worrell E, Price L, Galitsky C (2004) Emerging energy-efficient technologies in industry: case studies of selected technologies. Lawrence Berkeley National Laboratory, LBNL-54828, Berkeley

Worrell E, Blinde P, Neelis M, Blomen E, Masanet E (2010) Energy efficiency improvement and cost saving opportunities for the U.S. Iron and Steel Industry: an ENERGY STAR guide for energy and plant managers. www.energystar.gov/ia/business/industry/Iron_Steel_Guide.pdf, www.ceeindustrial.com/public/data/companyCatalogue1224056297.pdf

Xu EC (2001) P-RC alkaline peroxide mechanical pulping of hardwood, part 1: aspen, beech, birch, cottonwood and maple. Pulp Paper Can 102(2):44–47

Xu T, Slaa JW, Sathaye J (2010) Characterizing costs, savings and benefits of a selection of energy efficient emerging technologies in the United States. California, p 101

Yamaguchi A (1983) Operating experiences with the moxy process and quinoid compounds. In: Tappi pulping conference proceedings, Houston, October 24–26, pp 544–548

Yanhong G, Jing S, Qun L (2015) China's high-yield pulp sector and its carbon dioxide emission: considering the saved standing wood as an increase of carbon storage. BioResources 10(1):10–13

Yant R, Hurst MM (1991) Mill optimization using Monox-L as a replacement for chlorine dioxide. Tappi J 74(4):165–168

Young J, Start G, Lazorek J (1992) Utilization of an Eop stage during 100 % ClO_2 bleaching at Weldwood Hinton. In: CPPA Pacific and Western Branch annual meeting preprints, Technical section, CPPA, Montreal: Section 4A, paper No. 3

Zhou Y (2004) Overview of High Yield Pulps (HYP) in paper and board. In: PAPTAC 90th annual meeting, 2004, pp B143–B148 (Montreal, Canada)

Zhou Y, Zhang D, Li G (2005) An overview of BCTMP: process, development, pulp quality and utilization. China Pulp Pap 24(5):51–60

Chapter 5
State-of-the-Art Pulp Mills

Abstract Fiberlines that encompass "State-of-the-Art" technology and management practices are discussed. These include: Celulosa Arauco y Constitución S.A. Nueva Aldea, Chile; Veracel Celulose; Hainan Jinhai Pulp mill; Cellulosa Arauco Valdivia; Aracruz, Line C, Brazil; Mercal Stendal, Germany; Bowater, Catawba SC, USA; Zhanjiang Chenming Greenfield pulp mill, China; Eldorado Celulose e Papel S.A.'s new greenfield pulp mill in Três Lagoas, Brazil; Montes del Plata mill in Uruguay; Oji Holdings Nantong pulp mill Jiangsu Province, China; Aracruz's pulp line, at their Guaiba mill in Rio Grande do Sul, Brazil; Ilim Group's new kraft pulp mill, in Bratsk, Irkutsk Oblast, Russia; Metsa-Botnia, Rauma Mill; Metsa-Botnia Joutseno mil; Stora Enso's Nymölla Mill. Today's State-of-the-Art mills use less wood; are energy self sufficient; less polluting and provide sustainable value to society.

Keywords Pulp and paper industry • Pulp mill • Fibreline • Energy efficiency • Environmental impact • Productivity • State-of-the-art mills • State-of-the-art technology

Pulp and Paper industry is facing continuous pressure to improve energy efficiency, raise product quality, reduce environmental impact and maximize productivity. This has notably shaped bleaching and pulp production methods. Producers have responded to these demands by adopting efficient, low impact designs on economies of scale that far surpass most existing mills. Modern mills have less equipment, but are of significantly larger capacity than 20th century mills (Johnson et al. 2008, 2009a, b; Andrede 2011). New fibrelines have been built especially in Asia and South America. In these countries, access to fast growing raw material, other production cost advantages, stable politics and economies, and surging demand from the East give favourable levels of cost and return. Several mills and fibrelines that encompass "State-of-the-Art" technology and management practices have been started. Today's State-of-the-Art mills use less wood; are energy self sufficient; less polluting and provide sustainable value to society (www.aet.org).

State-of-the-art cooking includes both batch and continuous processes using low cooking temperatures and optimised alkali profiles (Gullichsen and Fogelholm 2000). Continuous cooking has been mostly used over the last decade. It typically consists of two-vessels for softwood and one- or two-vessels for hardwoods.

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The chip feed is of uniform quality. This results in reduced processing upsets. Lower cooking temperatures (145–153 °C) are typically used. Kappa numbers are in the range 17–22 for birch, 15–18 for eucalyptus and 26–35 for softwoods. Good impregnation is a key factor in obtaining good yield. The washing equipment and configuration are different for most mills. Compared with the previous generation of mills, atmospheric diffusion washers and drum washers have been replaced in modern mills by presses, CB filters and multi-stage DD washers that achieve high Equivalent Displacement Ratios (EDRs). Employing efficient wash equipment is very much important if a mill wants to achieve sustained bleach plant closure and filtrate recycling. This type of equipment ensures high dissolved solids recovery, minimum filtrate volume and minimum fibre content in the filtrate. To avoid calcium oxalate scaling and control bleaching chemical (particularly peroxide) consumption, pH control and metal ion management is required. Deknotting and primary screening can be performed in a single stage with knot separation and return to the digester chip bin via a blower system. Alternatively, recovered knots can be directly injected into the digesters. Deknotting and screening can be carried out before or after oxygen delignification. Screening after oxygen delignification has the following advantages:

- Less foaming
- Making the pulp easier to screen
- Higher yields due to breakdown of shives
- Smaller and cleaner rejects
- Heat balance advantages between the cooking and oxygen stages

Screening can be performed in either 3-stages or 4-stages. Rejects can be taken out of the system or recycled by washing and return to the oxygen delignification stage. Oxygen delignification is typically carried out at medium consistency and in two stages (Lindstrom 2003; Hart and Rudie 2012). In the previous decade, oxygen delignification was mostly conducted in one stage. The bulk of the delignification occurs in the first tower, which is typically run at lower temperature and higher pressure than the second reactor. The first reactor temperature is typically in the range 85–95 °C, at a pressure of 6–8 bar, and with addition of around 60–70 % of the alkali and oxygen charge. Some mills add all chemicals to the first reactor. Typically, the retention time in the first tower is around half that of the second tower. The second reactor temperature is 95–100 °C at a pressure of 3–5 bar (McDonough 1996; Lindstrom 1990). Temperatures and chemical charges are lower for hardwoods, reflecting the generally lower incoming kappa number compared with softwoods. The degree of delignification varies between 50–60 % for softwood, and 40–50 % for hardwoods. A significant portion of the hardwood "kappa number" is hexeneuronic acid which lowers the overall degree of delignification compared with softwoods (Vuorinen et al. 1999; Jiang et al. 2000). Kappa targets are set to preserve pulp strength and pulp yield. Magnesium sulphate is often added to preserve strength, particularly for softwood pulps (McDonough 1996). To conserve water, condensate from evaporation is sometimes used in the last stage of oxygen delignification for washing.

In the modern mills, elemental chlorine free (ECF) bleaching sequences are the standard for bleaching (Pikka et al. 2000; Johnson et al. 1996; Beca AMEC 2006; AET 2007; Nelson 1998; Nelson et al. 1995; Pryke 2003; NCASI 2003). Bleaching is performed in four stages. Modern bleach plants commonly operate with upflow towers in all stages, with interstage washing using drum displacer (DD) washers or presses. The washing is typically counter current with white water from the pulp machine being used for washing on the final stage washer. Variations to true counter current washing have been developed to reduce pH transitions and to create alkaline and acid purge streams to manage metals, extractives and scaling. The excess filtrates, both acid and alkaline, are often filtered to recover fibre before they are sewered. To reduce emissions of COD, BOD5 and colour from the bleach plant, it is possible to recycle the alkaline filtrate from the Eop stage (oxidative alkaline extraction using hydrogen peroxide) and use it for washing prior to the first bleaching stage (NCSU 2003; Beca AMC 2004; Chandra 1997). All mills have on-line analysers and optimisation controls. The control of final brightness is very accurate and quality downgrades are almost non-existent. Standard deviation of the final brightness is typically less than +0.5 % ISO. The bleach plants have a high level of on-line instrumentation that allows tracking, analysis and optimal control of the bleaching process to achieve consistent quality and cost efficiency.

The information on few state-of-the art mills – Celulosa Arauco y Constitución S.A. Nueva Aldea, Chile; Veracel Celulose; Hainan Jinhai Pulp mill; Cellulosa Arauco Valdivia; Aracruz, Line C, Brazil; Mercal Stendal, Germany; Bowater, Catawba SC, USA; Zhanjiang Chenming Greenfield pulp mill, China; Eldorado Celulose e Papel S.A.'s new greenfield pulp mill in Três Lagoas, Brazil; Montes del Plata mill in Uruguay; Oji Holdings Nantong pulp mill Jiangsu Province, China; Aracruz's pulp line, at their Guaiba mill in Rio Grande do Sul, Brazil; Ilim Group's new kraft pulp mill, in Bratsk, Irkutsk Oblast, Russia; Metsa-Botnia, Rauma Mill; Metsa-Botnia Joutseno mil; Stora Enso's Nymölla Mill – are presented below:

5.1 Celulosa Arauco y Constitución S.A. Nueva Aldea, Chile

Nueva Aldea is a model for environment-friendly operation and is a gleaming example of a modern pulp mill (Rodden 2007) (Fig. 5.1). This mill started in mid-September 2006, and has an annual production of 856,000 tonnes of kraft pulp (Wold 2008). The mill consists of two continuous fibre lines. One is for production from eucalyptus nitens and eucalyptus globulus and another is for production from radiata pine. 50 % of the production is hardwood and 50 % softwood. Both qualities are fully bleached. Metso Paper supplied the mill with two parallel pulp drying lines with three complete baling lines. Pulp drying line included rescreening, wet end,

Fig. 5.1 Nueva Aldea, Pulp Mill, Chile (Rodden 2007. Reproduced with permission)

airborne dryer, cutter lay boy and pulp baling systems and designed to minimize consumption of water, steam and electrical energy. The machinery operates in a closed system, returning all of its emissions back to other processes in the fibre lines. Metso Paper supplied two complete fibre lines featuring the latest technology in continuous digesting, Compact Cooking G2 process. This process uses a high liquor to wood ratio, which produces a much more uniform pulp. The liquor to wood ratio in Nueva Aldea's digesters is 4–5:1 compared with the normal 2.7:1. Pulp quality is high at an average brightness of 92 ISO. In terms of production, each line produces the guaranteed 1,300 ADT/day. Except for a small amount of purchased chips, all of the wood used comes from Arauco's own plantations. The pine and eucalyptus are separated in the woodyard. However, the two species of eucalyptus are mixed after chipping. Hardwood yield is 53–54 %, softwood, about 48 %. Hardwood and softwood lines are separated in the woodyard. Only the recovery area is common. Kvaerner Pulping supplied both fibrelines while Kvaerner Power supplied the power and recovery boilers. Both units are now part of Metso Paper, which additionally supplied the two parallel pulp dryers as well as three baling lines. Andritz supplied the woodyard, limekiln and causticizing unit. Emerson provided the Delta V distributed control system, while Metso Automation supplied the pulp analyzers and valves. On the chemical side, Aga supplied the oxygen system while Akzo Nobel chlorine provided the chlorine dioxide plant. The eucalyptus bleaching sequence features hot chlorine dioxide in the first stage. The sequence is D0EOPD1D2. There is a GL&V (formerly Kvaerner Pulping) Compact Press between the D1 and D2 stages. Pulp enters the dryer at 53 % dryness and exits at 90 %. Nominal speed of the dryers is 250 m/min. As with most kraft pulps, Nueva Aldea is energy self-sufficient and is able to sell 35 MW back to the grid. Water consumption is running about 30 m^3/tonne. The mill's efficiency goal is 93. Recently, Nueva Aldea pulp mill has upgraded their bleach plant by two Valmet TwinRoll wash presses. One press is placed between the first stages of the bleaching sequence, between the D0 and EOP stages, while the other one is installed after the D1 stage. The presses are designed for a production of up to 1,580 tonnes/day and a pulp feed consistency of 7 %. The main advantages of the new presses are the high availability, the high output consistency and the low consumption of chemicals.

5.2 Veracel Celulose

Veracel Celulose S.A. engages in the forestry and pulp mill businesses in Brazil. Its forestry operations comprise interests in approximately 164,600 ha of land distributed in ten municipalities in the south of the state of Bahia. It primarily focuses on eucalyptus plantations. The company also operates pulp mills; and produces pulp and paper. The company was formerly known as Veracruz Florestal Ltd. and changed its name to Veracel Celulose S.A. in 1998 (www.veracel.com). Veracel Celulose S.A. was founded in 1991 and is based in Eunapolis, Brazil. The company is a subsidiary of Stora Enso Corp. and Fibria Celulose SA. Veracel is considered to be one of the top performing bleached hardwood kraft mills in the world. Investment for the mill $US 860 million Started up May 2005. Veracel Celulose is located in the extreme southern portion of the Brazilian state of Bahia. The area, rich in eucalyptus, is one of the largest and productive plantations in the world. Andritz, supplied fibre line, drying machine, causticising plant, rotary lime kiln. Chemical plant was supplied by EKA Chemicals; Confab supplied falling-film type evaporation in six stages, Aker Kvaerner supplied recovery boiler and auxiliary boiler using bubbling fluidizer bed technology, Mitsubishi supplied turbine-generator and ABB supplied electrical power distribution system.

Veracel Celulose, eucalyptus mill uses 2-vessel vapour-phase Lo-Solids® continuous cooking, and a hot chlorine dioxide ECF bleach sequence (Johnson et al. 2008, 2009a, b) (Fig. 5.2). The mill has a design capacity of 900,000 adt per annum but actual production has consistently exceeded this target. Eucalyptus urograndis is the main species used. Production in 2007 was in excess of 1,050,000 adt.

Veracel operate continuous pulping systems. Veracel's low level – Lo-Solids cooking system consists of an hydraulic impregnation vessel and a steam-phase digester. The main objective of the Lo-solids cooking is to increase the selectivity of the cook through low and uniform radial cooking temperatures and a uniform alkali profile. Cellulose dissolution is minimised in the principal and residual delignification phases, and relatively high yields of around 55 % OD are achieved. Veracel has two parallel pressurized diffusers after the digester followed by 2-stage DD washers prior to oxygen delignification. Deknotting and screening can be carried out either before oxygen delignification, or after. Veracel claims advantages in screening after oxygen delignification. Deknotting and primary screening occur in a single stage. Veracel operates two parallel ModuScreen units for knots separation

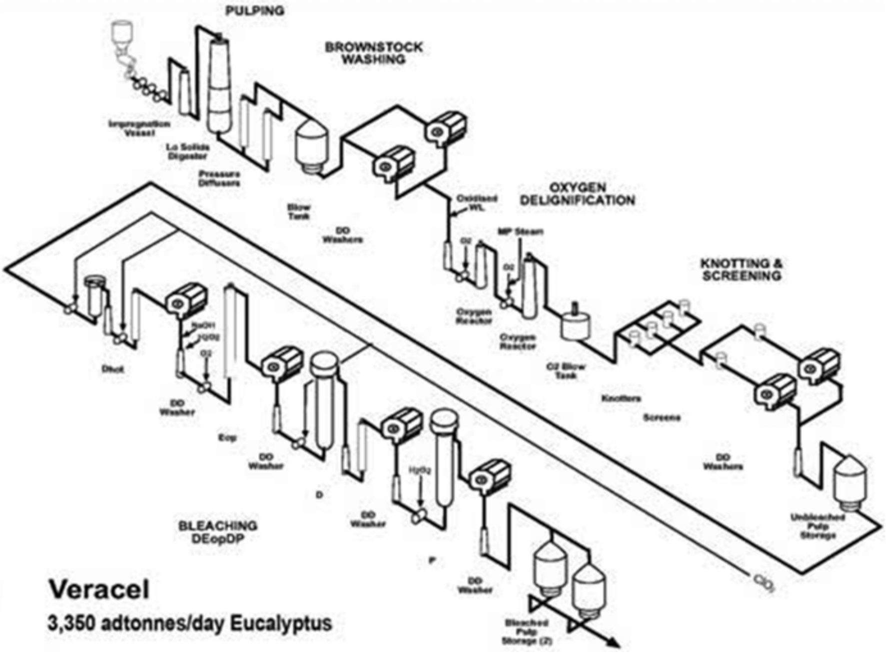

Fig. 5.2 Veracel fibre line (Johnson et al. 2009b. Reproduced with permission)

and primary screening, followed by washing and return of knots to the digester. Screening is 3-stage and the options with rejects are to recycle; they are cleaned, washed and returned to the oxygen delignification stage, or landfill them. Veracel is using two stage oxygen delignification. It runs its first reactor at a temperature of 92–96 °C, a pressure of 6–8 bar, with the addition of 60–70 % of the alkali and oxygen charge. Veracel operates the second reactor at a temperature of 98–100 °C and a pressure of 3–5 bar. The degree of delignification varies between 60 % for softwood, and 40 % for hardwoods. Veracal is using 4-stage bleaching sequence. The original bleach sequence of Veracel was A/D0 (Eop) D P which was modified after start up to Dhot (Eop) D P. This resulted in a significant reduction in chemical consumption. Veracel's bleach plant operates with upflow towers in all stages followed by a DD washer after each tower. The washing is counter current with filtrate from the pulp machine being used for washing on the final DD washer. Veracel, has very low bleach chemical consumption. The two first stages have displacement presses and the last two stages have simpler dewatering presses. Hot water is used for Eop washing, and pulp machine filtrate is used before the last D stage press. A minor amount of cold water may be added to the dilution before the first D stage for temperature control. The excess filtrates, both acid and alkaline, are filtered before they are sewered. To decrease emissions of COD, BOD and colour from the bleach plant, it is possible to recycle the alkaline filtrate from the Eop stage and use it for washing prior to the first bleaching stage. This mill claims to have the lowest chlorine dioxide consumption in the world. It is using online Kajaani analyzers and bleach plant optimization controls provided by Metso Automation. The low level of chemical usage means lower costs of production. Moreover, the control of final product brightness is so precise that quality downgrades are virtually non-existent. To ensure this consistent quality and cost efficiency, the mill uses a high level of online bleach plant instrumentation that allows it to track, analyze and optimally control the bleaching process. Veracel Celulose is using HPD® black liquor evaporation system, designed by Veolia Water Technologies and installed by Confab Equipamentos S.A. (www.veoliawaterstna.com/news-resources/…/veracelhp-devaporators.htm). The system has achieved and maintained the specified rates and capacity since commissioning. The condensate segregation system has produced the quality of water required for optimal reuse in the mill.

The environmental performance for the Veracel mill has been well within the internal targets and the Best Available Technology (BAT) references. Veracel is probably the only mill that discharges its effluent upstream of its intake, which is a requirement of the mill's operating licence. Effluent is treated in an activated sludge process and solid wastes are used to produce organic compost. The mill is believed to be amongst the best in the world in terms of effluent and air emissions, operating at approximately 50–75 % of the legal limits. Water consumption is in the range of 22–24 m^3/tonne of pulp, with BOD and COD limits set at 0.3–0.4 kg/tonne and 5 kg/tonne, respectively. Atmospheric emissions are permanently monitored. There is one common stack for all air emissions. Emission control technology includes high efficiency electrostatic precipitators, an odorous gases collection system, and stripping of foul condensates which are collected and burnt in the boilers.

5.3 Hainan Jinhai Pulp mill

Hainan Jinhai Pulp mill is located on Hainan Island in southern China. It produces 1 million tonnes/year of bleached hardwood kraft pulp. It is the world's largest single-line pulp mill and is China's first large-scale fibre line (Rodden 2006; Johnson et al. 2009a, b). Its recovery boiler can handle 6,000 tonnes/day of dry solids. Environmental standards for the mill are strict as Hainan Island is a popular tourist destination. The mill is aiming to keep effluent emission levels below the imposed standards. Hainan Jinhai produced its first pulp in November 2004. The mill's fibre supply is Eucalyptus grandis and Acacia crassicarpa, in approximately equal volume and is sourced internally from plantation forests. The mill's fibre is eucalyptus and acacia, split about evenly. Presently, about 20 % of the mill's fibre is purchased; the rest comes from APP's plantations. About half of the wood is delivered as chips. The mill's production is used to supply pulp to the several APP paper machines in China.

Major suppliers to the project included Kvaerner Pulping and Kvaerner Power, ABB, Siemens, Andritz, Foster Wheeler, BTG, Veolia Water-unit HPD (six-effect,

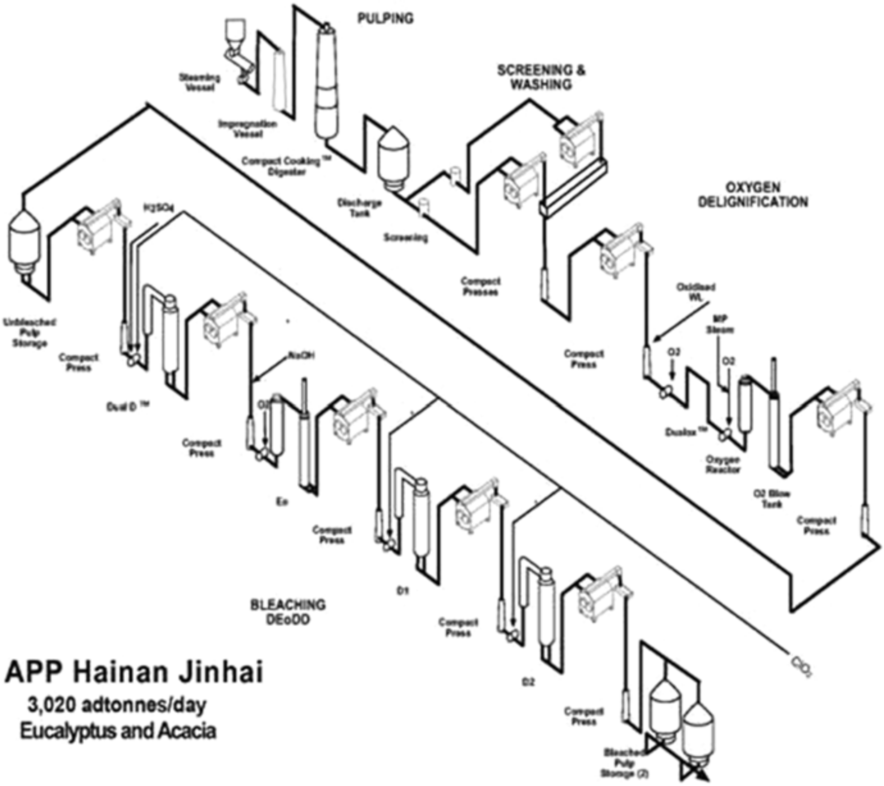

Fig. 5.3 Hainan Jinhai pulp mill (Johnson et al. 2009b. Reproduced with permission)

falling film evaporators), FL Schmidt (lime kiln), Rexroth (digester motor), Hagglunds (motors), Sulzer Pumps and Aker Kvaerner Chemetics (chlorine dioxide generator). Andritz supplied woodyard/wood processing and pulp dryer/baler. The woodyard is the world's largest. It can handle 1,160 m^3/h of solid wood. There are four wood receiving and chipping lines (Rodden 2006). Each line has a feeder deck, conveyors and gravity-fed HQ-Chipper (Fig. 5.3). The feeder deck operates without conventional chains, making maintenance easier. The chippers are designed to produce high quality chips even with the small diameter logs the mill has available. Stone traps, metal detectors and other devices ensure that clean chips are sent to the fibre line. The chips are stored in two open piles, each containing 150,000 m^3. Four CantiScrews under each pile reclaim the chips and send them to screening: this is the JetScreen system in which dust, fines, oversize and overthick chips are separated from accept chips with air impulses. The oversize and overthick chips are sent to an HQ-Sizer for reprocessing prior to cooking. Rejects are used as fuel in the power boiler (Rodden 2006). The pulping process uses Compact Cooking from Kvaerner Pulping. Following the steam bin, the chips go through a high-pressure feeder

(Compact Feed). The system does not break the chips but feeds them into the liquor impregnation vessel which is as big as a conventional digester. The digester is one of the largest pressure vessels of its type with a bottom diameter of 12.5 m. It is 71 m high and the retention time is 6 h. Both the impregnator and digester are downflow. The digester takes about 30 m^3 of chips per minute. After cooking the pulp is sent to a blow tank. After that it is pumped to a high-pressure screening system to remove any knots. The system is set up for two-stage screening but the mill generally needs to run only one stage. APP China has made extensive use of Kvaerner Pulping's Compact Press technology with nine units in place. In the brownstock line, the presses help reduce COD carryover and soda loss into the bleach plant. The advantage of the presses in the bleaching process is low water consumption. The first two Compact Presses are in parallel, after the screening stage. Pulp enters the press with 3.5 % consistency. It is the only place where there are two parallel presses. The pulp then passes to a third Compact Press. This mill is using Dualox process (two-stage oxygen delignification). The retention time in the second stage is 1 h. The pulp is then washed and sent to a medium consistency (10 %) tower (7,000 m^3 capacity). Following the fifth Compact Press, the pulp is ready for bleaching. The process is the DualD using hot chlorine dioxide. There are upflow/downflow towers in each D stage. Retention time can be controlled making the process easier to operate. There are Compact Presses for washing after each stage. Brightness is up to 89 ISO. The bleached pulp is sent to one of two high-consistency storage tanks, each with a capacity of 11,000 m^3. The pulp dryer at Hainan Jinhai is the world's largest. Prior to the pulp machine, there is an ModuScreen screening system, arranged in a closed cascade design to achieve high efficiency. The pulp dryer uses twin-wire forming technology. A three-roll Combi-Press followed by a double-felted shoe press results in good dewatering. In the Flakt air dryer, there are no moving mechanical parts inside the drying chamber except for turning rolls at either end of the machine. After the cutter/layboy, there are four automated baling lines. The mill makes its own wrapping. Approximately $250 million was spent on environmental protection. There is a three-stage effluent treatment plant: primary, secondary and biological. Sludge from the treatment plant is dried and pressed to about 70 % moisture and then burned in the power boiler. All non-condensible gases from the fibre line are collected in a closed system and burned in the recovery boiler. The gases from the bleach plant are collected, passed through a scrubber and released. Dust from the boiler and limekiln is treated in an electrostatic precipitator before being released. The mill is energy self-sufficient. Although it is connected to the national grid, it operates as an island. Its self-sufficiency is helped by the world's largest recovery boiler, which can produce 204 kg/s of steam at 84 bar and 480 °C. The Kvaerner Power unit has a multi-level air system to ensure consistent combustion. It is also designed to give low emissions of carbon monoxide, total reduced sulfur and NOx. The Foster Wheeler power boiler burns coal, bark, pin chips and other waste. The mill can produce 1,000 tonnes of steam/h, 30 % of which comes from the power boiler, the rest from the recovery boiler. Siemens supplied the three steam turbine generators and also the complete electrical engineering system for the mill.

5.4 Cellulosa Arauco Valdivia

Valdivia Cellulose Pulp Plant is located in San Pedro de La Mariquina 56 km northwest of Valdivia in southern Chile (Fig. 5.4). It started in February 2004. The mill is owned by Cellulosa Arauco y Constitucion S.A. (CELCO-Arauco) and produces 550,000 tonnes pulp per year for international exportation. Valdivia is a 'swing' mill producing both radiata pine (60 % of production) and eucalyptus pulp. The mill design and vendor equipment packages are based on a maximum capacity rate of 1,700 ad tpd for pine and 1,900 ad tpd for eucalyptus. E. nitens (70 %) and E. globulus (30 %) are the eucalyptus species pulped (Johnson et al. 2008, 2009a, b). The mill is located in an environmentally sensitive area, especially with respect to air and water emissions. Very low loadings to the recipient waters are a key requirement, which are achieved by a combination of process selection and operational control. Concentrated and dilute non-condensible gases from the fibreline, evaporation and causticizing plants are collected, treated and incinerated in the recovery boiler. Effluent treatment consists of primary, secondary and tertiary treatment stages followed by disk filtration to minimise suspended solids prior to discharge. Arauco Valdivia's bleaching sequence is a conventional ECF sequence, D (Eop) D D. The first bleaching tower is upflow, with a top scraper and a dropleg to the MC pump standpipe (Fig. 5.5). The three other towers are upflow-downflow, with MC bottom. The upflow section of the Eop tower is a pressure vessel. Mixers are all dynamic type SMD-300 in all stages. Washing is with wash presses. The two first stages have displacement presses and the last two stages have simpler dewatering presses. Hot water is used for Eop washing, and pulp machine filtrate is used before the last D stage press. A minor amount of cold water may be added to the dilution before the first D stage for temperature control. The excess filtrates, both acid and

Fig. 5.4 Celulosa Arauco y Constitucion's new facility in Valdivia Province, Chile (Rodden 2005. Reproduced with permission)

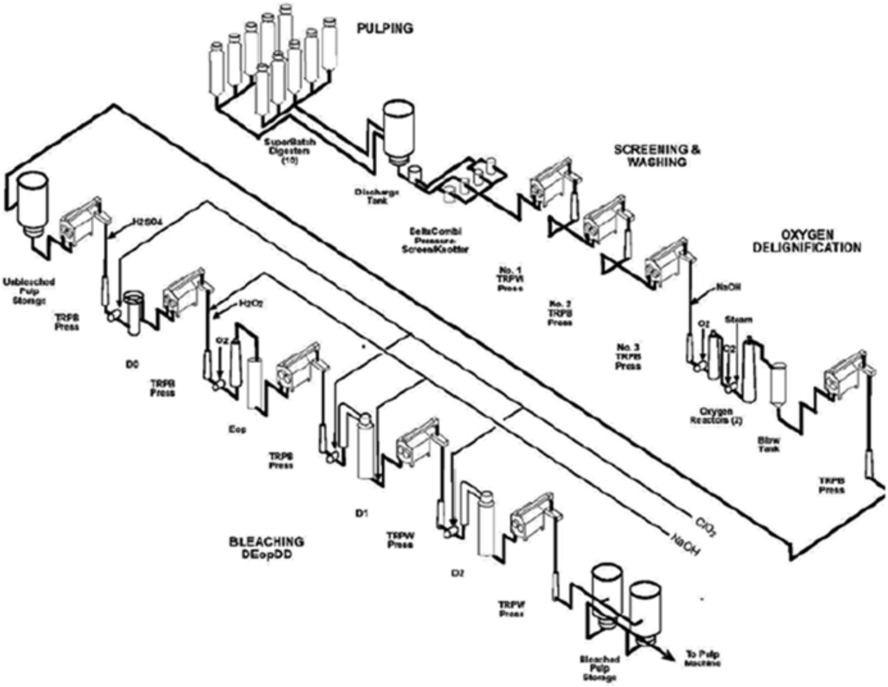

Fig. 5.5 Arauco Valdivia fibre line (Johnson et al. 2009b. Reproduced with permission)

alkaline, are filtered before they are sewered. To decrease emissions of COD, BOD and colour from the bleach plant, it is possible to recycle the alkaline filtrate from the Eop stage and use it for washing prior to the first bleaching stage. Figures 5.6 and 5.7 show Super Batch digesters and TwinRoll Presses Valdivia mill respectively.

The Arauco Valdivia mill is located in an environmentally sensitive area, and based on some benchmarking of its permit, have some of the most stringent effluent limits for bleached kraft pulp mills anywhere. Valdivia has three permits that cover all parameters. The mill is in compliance with its permit targets. The Valdivia effluent treatment system treats three main mill streams: the low solid sewer which includes bleach plant effluents and excess evaporator condensates; the general mill sewer including effluent from landfill and the woodyard; the storm water system. The main features of the treatment system include:

- A spill pond with spill pumps (130,000 m^3)
- Primary treatment for the main sewer including an automatic screen, primary clarifier, scraper, and fibre sludge pump
- Neutralisation stage, and cooling towers (two chambers)
- Secondary treatment (two parallel lines)
- Aerated basins, nutrient addition, secondary clarifiers, scrapers, and fibre sludge pumps

Fig. 5.6 Super batch digesters at Cellulosa Arauco Valdivia (Rodden 2005. Reproduced with permission)

- Tertiary treatment (parallel lines) – flocculation chambers, chemical addition (alum, polymer, peroxide), scrapers, and sludge pumps
- Disc filters (three) in parallel, to reduce hansuspended solids
- Cooling towers to control the final effluent temperature
- Sludge handling system including two belt filter presses for sludge dewatering.

Toxicological studies of acute toxicity and chronic toxicity have showed no impact in the recipient (river) environment. No lethal effects were detected for the species H. gracilicornis, D. obtusa, G.. affinis. y O. mykiis, nor any chronic toxicity in L. valdiviana, S. capricornotum, G. affinis y O. mykiis. Arauco Valdivia both use a tertiary flocculation stage to remove additional organic material. This results in very low COD and AOX levels in discharged effluent in comparison to biological treatment alone, but incurs the expense of additional chemicals, and sludge handling and disposal. Sludge disposal options include land application or incineration. The use of additional chemicals may also increase the discharge of inorganic salts in the final effluent. Tertiary treatment is considered in cases where receiving waters are of poor assimilative capacity, or otherwise restricted, and, as such, is identified as a supplemental or optional technology in recent BKP best technology reviews (Beca AMC 2004).

5.5 APRIL/SSYMB Rizhao Greenfield Mill

APRIL SSYMB Rizhao mill, is situated in the heart of Rizhao city. The mill is a joint venture between APRIL (Asia Pacific Resources International) and local government. All main processes for kraft pulp production and chemical recovery was supplied by Valmet. Valmet also provided supervision services for erection and

Fig. 5.7 Twin roll presses at Cellulosa Arauco Valdivia (Rodden 2005. Reproduced with permission)

start-up, as well as training of mill staff. On June 30, 2010, the mill produced it's first pulp sheet. The mill has a state of the art ecofriendly and odorless production. The Rizhao mill is designed for very low energy, water and chemical consumption (www.valmet.com/en/products/pulping…/WTB-110628-2256F-F0632?).

Compared to any other pulp mill built in recent times, it has the lowest impact on the environment. The target is to eliminate solid waste from the mill. The mill has invested in the best available technologies to eliminate smell and reduce the colour of effluent, and minimize solid waste. "This mill is the new benchmark in size and performance for the pulping industry," says APRIL COO A. J. Devanesan. Acacia and eucalyptus wood are the raw material for pulp production. The chips are stored in five GentleStore circular chip storage systems, each designed for a capacity of 190,000 m^3. The fibre line comprises equipment and processes for cooking, pulp screening, brownstock washing, oxygen delignification and bleaching. The selected technology features Valmet's continuous CompactCooking, Delta screening and TwinRoll wash presses installed for each stage of pulp washing. An ECF sequence O-DHT–EOP–D-D/P was selected for pulp delignification and bleaching. The new CompactCooking method produces pulp with higher yield, better bleachability and lower energy consumption than other cooking methods. Pulp drying is carried out using Valmet's energy-saving DryWay concept. The process at the APRIL/SSYMB mill consists of two parallel drying lines. The trim width of the drying machines is eight meters. The delivery encompasses all necessary process systems from re-screening, drying and cutting through to ready-made bales. Valmet's twin-wire DryWay concept furnished with two shoe presses enables high web dryness prior to the airborne dryer and thereby remarkable energy savings. After pulp drying and cutting, the sheets are baled in three baling lines installed for both lines. Valmet's Robobaling technology is used for pulp baling. Both baling systems share two unitizers from where the bale units are transported to storage.

Black liquor from the pulping system is evaporated in Valmet's EVAPS plant including two parallel evaporation lines, each dimensioned for evaporation of 1,000 tonnes of water per hour. The liquor at approximately 80 % dry solids content is burned in Valmet's RECOX boiler which is designed for a maximum capacity of 7,000 tonnes of dry solids per day. Strong and weak odorous gases are burnt in the recovery boiler. During June 2010, the boiler was run for few days with 7,550 tDS/day – the record firing capacity in the world. APRIL is the largest tree planter in the world. It is also the largest hardwood market pulp supplier in Asia and the second largest globally. The company produces paper under the brand name PaperOne, which is sold as a premium product in over 60 countries.

5.6 Aracruz, Line C, Brazil

Fibreline C was started in 2002 which increased the Aracruz's production from 1.3 million to two million tonnes of pulp per year. Andritz was a major supplier of process technology and systems for the Fibreline C project. Andritz supplied Woodyard, Fibreline (excluding digester), Recausticizing/Kiln, Pulp Dryer (with Voith Paper/ ABB/Moura Schwark), Automated Baling Lines. Fibreline C has the capacity to produce special ECF pulps for printing/writing, hygienic, photographic, and papers for digital printing. Kvaerner Pulping supplied cooking and washing equipment. Compact CookingTM is used which provides greater strength and higher yield while reducing chemical consumption (Knight 2002). The strength of the pulp is higher in comparison to the pulp of other lines. Part of the strength improvements are achieved in the cooking process and part in the bleaching process. The processes include oxygen delignification, ECF bleaching, closing the effluent loops in the second and fourth bleaching stages, reusing water from the dryer in bleaching, and a system of collection and recovery of spillage in all areas. The bleaching sequence used is ADO-Eop-DnD sequence. Design capacity is 2,200 admt/day. Pulp can be bleached to 92 ISO brightness. Patented AhlStage technology is used to lower bleach plant chemical consumption. The new line gives Aracruz flexibility to produce pulps for various paper grades. Aracruz is reducing water consumption through new equipment and processes. Fibreline C will consume about 18 m^3/t of pulp produced. The fibreline equipment contributes significantly to reduced water consumption. Odorous gas emissions will be around 2 ppm of

Fig. 5.8 The twin-wire pulp machine at Aracruz Celulose S.A.'s new C line at its Barra do Riacho mill (Knight 2002. Reproduced with permission)

total reduced sulfur (TRS). Fibreline C also has a latest generation system of gas incineration for the entire complex. This system prevents emissions of odorous gases which, after being treated, are burned in the recovery boiler. About half of line C's output will be used to make tissue. The rest will be split evenly between specialty papers and printing and writing grades.

Figures 5.8 and 5.9 show the Twin-wire pulp machine and the Recausticizing plant respectively.

5.7 Mercal Stendal, Germany

The Stendal mill is a state-of-the-art, single-line NBSK pulp mill situated near the town of Stendal, Germany with a current annual pulp production capacity of approximately 645,000 ADMTs. Metso supplied the complete fibreline, from wood handling to finished bales, as well as a millwide automation system (Toland 2004). The black liquor evaporation plant (670 tonnes/h), recovery boiler (3,250 tonnes dry solids/day) and recausticizing plant (8,000 m^3/day) was supplied by Andritz. Other key suppliers included Purac (biological water treatment), Sulzer Pumps (pumps and agitators) and Wiessner (air engineering). Stendal Fibre line system has Twin roll wash presses in each washing stage. Figure 5.10 shows the Evaporation plant.

Stendal is PEFC-certified and sources wood exclusively from sustainable forests within a 300 km radius of the mill, as well as using chips from sawmills. The mill aims to use 70 % own-produced chips and 30 % from outside. There is three weeks roundwood storage space on site.

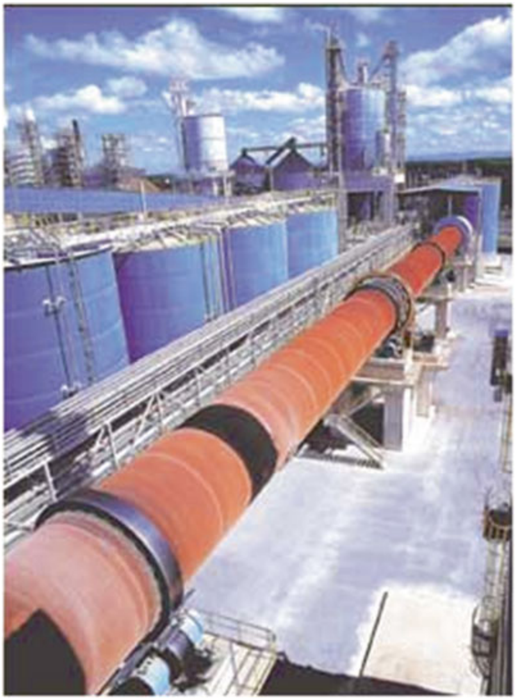

Fig. 5.9 Recausticizing plant at Aracruz Celulose S.A.'s new C line at its Barra do Riacho mill (Knight 2002. Reproduced with permission)

Fig. 5.10 Evaporation plant at Stendal (Toland 2004. Reproduced with permission)

Stendal's pulp is produced from 70 to 80 % pine, 20 to 30 % spruce. ZS Holz which is a subsidiary company is responsible for wood procurement. ZS Transport, a second daughter company is responsible for both internal logistics and wood chip transport and product shipments to all markets. The logs are processed using Metso ChipWay technology, consisting of two debarking and chipping lines. Each line can handle up to 300 m^3 solid wood/h. The wood infeed system – GentleFeed – conveys the logs into the debarking drum on top of moving lamellas, rather than using chains or sprockets, the aim being to eliminate wood breakages and improve yield and chip quality, thereby decreasing the need for bleaching chemicals. Together with the infeed system, the Easy Tyre debarking drums and Camura GS chippers are designed to minimize wood losses and maximize the uniformity of chips destined for the digester. The mill also has a bark press that is used in winter when the bark is less dry. Unused bark is stored and then burnt in the bark boiler to generate energy. Stendal's bark and recovery boilers between them generate 90 MW energy. Since the mill needs only 55 MW, the remainder is sold to electricity suppliers. The mill is an "industry leader" in terms of efficient production and good environmental performance. Only chips of the right size and quality are made into pulp; those that are too large are rechipped, while fines go to the bark storage area prior to being burnt in the bark boiler. Chips produced on-site and those brought in from sawmills are stored in separate 60,000 m^3 chip piles for quality control reasons. Stendal employs Metso's SuperBatch pulp digesting process, including eight 400 m^3 digesters, together with pressurized accumulators and tanks for black, white and displacement liquor. After cooking, knots and shives are separated using four-stage DeltaCombi screening. The pulp is then further delignified in a two-stage OxyTrac oxygen delignification process. Bleaching is in four stages with washing by Twin Roll wash presses after each stage: the sequence for ECF pulp is Q-OP-D-PO; for TCF it is Q-OP-PAA-PO (Metso 2005). Stendal was initially conceived as a TCF-only mill, but they are producing both ECF and TCF pulp, with more of a focus on ECF. The storage area at Stendal can hold around 20,000 tonnes at any one time, or approximately 12 days' storage once the mill hits its target output of 1,700 tonnes/day. All the pulp Stendal is producing is basically the same. End-uses for Stendal's NBSK include printing papers, tissue papers and white packaging grades.

5.8 Bowater, Catawba SC, USA

State-of-the- art Bowater's Fibreline at the Catawba site was started in 2003, This Fibreline offers top-tier quality, environmental performance for bowater (Shaw 2004). It is designed to produce 1,500 tpd of bleached pine pulp for use in lightweight coated papers. Figure 5.11 shows the Catawba mill's fibre line design. The new fibre line can provide pulp that has improved optical and strength properties, using the latest technologies advantageous to the environment. This allows Bowater to compete more effectively in the North American and European tissue and towel and food packaging segments. In late 1999, the Catawba mill was faced with eliminating

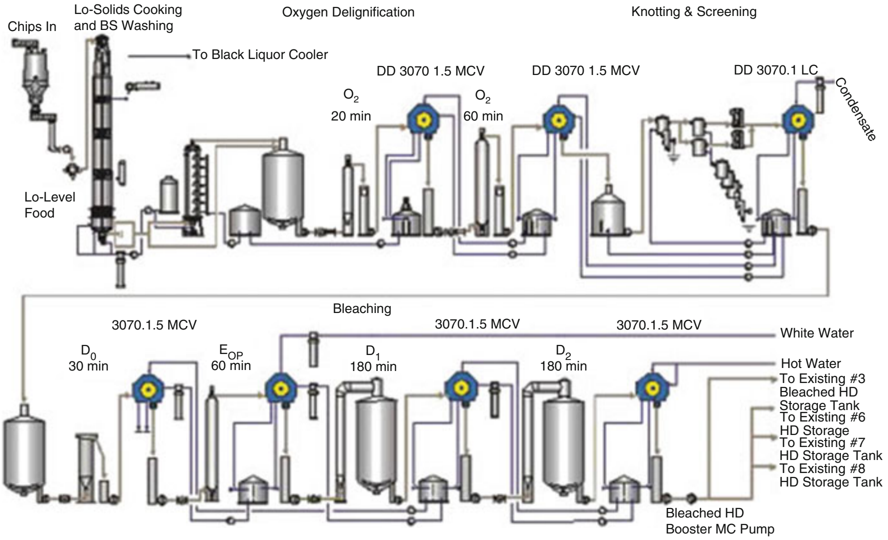

Fig. 5.11 Fibre line at Catawba (Shaw 2004. Reproduced with permission)

elemental chlorine and reducing AOX emissions from its bleached kraft fibre line. A major modification to the existing line might have met Cluster Rule compliance, but Bowater preferred to explore the long-term advantages of a completely new fibreline that would guarantee compliance. From an environmental point of view, a new fibreline would require less water and steam for the process resulting in reduced operating costs. The advanced technology has given Bowater Tier I Cluster Rule status with very low AOX discharge. Also, the new fibre line allows the use of less wood fibre and chemicals and provides a better quality pulp. Higher strength properties were important to Bowater's expanded emphasis on coated paper grades within the Coated and Specialty Papers Division especially with the conversion of the No. 3 paper machine from newsprint to coated paper. A turnkey EPC project was awarded to a consortium of three companies (AMEC/Andritz/Kamt) in December 2000. The fibre line design included a continuous digester (Fig. 5.12) featuring a low solids cooking method and brownstock washing to replace ten existing batch digesters. After the continuous digester comes a pressure diffuser, followed by two stages of oxygen delignification, each of which is succeeded by washing in a new, multi-stage drum displacement pressurized washer. Next, brownstock is screened, knotted, and washed again prior to bleaching. The selected bleaching equipment included a ECF, four-stage bleach plant that features a D0-Eop-D1-D2 sequence with the capability for n-stage bleaching between stages D1 and D2. Each bleaching stage is followed by washing in new, multi-stage pressurized washers. After bleaching, pulp is sent to one of four existing high-density storage tanks. Andritz DD washers are used from pre-oxygen to the end of the bleach plant. In addition, the project included a new chip conveyor leading to the fibreline that would be built around existing lines. Also included was a new, state-of-the art control room featuring a

Fig. 5.12 Continuous digester, Catawba's new fibre line, uses low solids cooking for lowest kappa number and highest fibre quality (Shaw 2004. Reproduced with permission)

new distributed control system. Presently, the new kraft pulp line consistently produces bleached kraft pulp at brightness levels of 89–90, with TAPPI dirt count of 1 or less. Pulp strength is good, as evidenced by record paper production, and it is improving all the time. The combined strength parameter has improved about 10 % already and continues to increase. In addition, water use and steam use have been reduced by about 25 %. Due to oxygen delignification, chemical consumption in the bleach plant is much less. The kappa number going into the bleach plant significantly reduced from around 30–14 with the use of two-stage oxygen delignification stage and low solids cooking in the continuous digester, along with advanced washing technologies. With no increased chlorine dioxide requirement in the new DEOPDD bleach plant, the mill was able to use its existing chlorine dioxide generation capacity. It could also retain its existing chemical recovery island with a few minor upgrades. Because oxidized white liquor was to be used in the two-stage oxygen delignification towers, about 30 % more was needed than before. A new burner was fitted in the lime kiln to achieve this and automated causticizing efficiency controls were installed in order to ensure sufficient white liquor production and a correct sulphidity balance in the mill. Because the new pulp mill and bleach plant operate considerably more "closed" than its predecessor, a new cooling tower was also installed. Overall, the new fibreline uses about 2 million gal of water/day less than the old pulp mill (20 % reduction/tonne of pulp). The effluent colour also improved. Among the water reduction measures implemented in the project was use of paper machine white water for washing in the bleach plant EOP stage. The mill has an effluent colour removal plant on site that ran all the time with the old pulp mill. But since startup of the new fibreline, it has not been used at all. Effluent colour has been more of a discharge limitation than anything else. AOX has been well within the limits since startup of the new fibreline.

5.9 Zhanjiang Chenming Greenfield Pulp Mill, China

Zhanjiang Chenming pulp mill is located in China's Guangdong Province. It reached the nominal production capacity of 700,000 tonnes/a in world record time – only 121 days from start-up. It has also produced 100 % of the design capacity during the first full operating year, thus achieving another world record (PPI mills and technology 2012). All key production technologies and start-up supervision were provided by international technology Group Andritz. Zhanjiang Chenming Pulp & Paper is a subsidiary of Shandong Chenming Paper, one of the largest pulp and paper producers in China. Andritz was awarded the contract to deliver all process technologies for the bleached hardwood kraft pulp mill located in Guangdong Province. The mill was started up in September 2011 and reached its nominal average production capacity only four months later (measured as a 30-day moving average). This represents a new "world record" based upon officially available figures of greenfield pulp mills. This extremely fast start-up has an important economic element in that it greatly enhances a mill's return on investment. Andritz supplied included the wood handling system, the fibreline (cooking, washing, screening, bleaching, pulp dryer, and bale finishing), and the recovery island (evaporation, recovery boiler, and white liquor plant) (Andritz 2012).

5.10 Eldorado Celulose e Papel S.A.'s New Greenfield Pulp Mill in Três Lagoas, Brazil

Eldorado Celulose e Papel pulp mill is based in the city of Três Lagoas, in the state Mato Grosso do Sul. This is the largest single-line pulp mill in the world, with capacity to produce 1.5 million tonnes of bleached pulp per year (www.valmet.com/valmet/products/…nsf/…/Results313Eldorado.pdf). The mill has been designed to optimize the energy balance and maximize electricity produced from biomass. The pulp is delivered to customers in Brazil and also exported to paper producing markets in South America, North America, Europe, and Asia. The recovery boiler combusts 6,800 tonnes of black-liquor dry solids per day and generates 1,109 tonnes of steam an hour. Andritz supplied woodyard, complete fibreline – cooking, washing, screening, and bleaching systems, pulp drying equipment and baling lines, as well as the white liquor plant with recausticizing and lime kiln and Metso supplied recovery boiler and evaporation plant. The mill will produce 1,600,000 tonnes/a bleached eucalyptus. The recovery boiler has a capacity of 6.800 tonnes of dry solids per day (tDS/day) and steam generation of 308 kg/s. The evaporation plant has six thermal stages and capacity of 1,600 tonnes per hour.

5.11 Montes del Plata Mill in Uruguay

Montes del Plata, the pulping company owned jointly by Stora Enso and Arauco, officially inaugurated its greenfield mill near Punta Pereira, Uruguay on September 8, 2014 (www.storaenso.com/…/inauguration-of-stora-enso's-joint-operation-pulp..). The design capacity for the mill is 1.3 million tonnes of bleached eucalyptus pulp per year. Andritz delivered key production lines for the mill. Andritz was also responsible for the civil construction, erection, commissioning, and start-up of these production lines (Andritz 2014). The pulp will be produced using ECF bleaching with low chlorine dioxide consumption (ECF-Light) from plantation grown eucalyptus trees. The main processing units of the pulp mill will include the following: wood yard; digester; oxygen delignification; ECF bleach plant; pulp dryers; evaporators; recovery boiler, turbogenerators and recausticizing (i.e. chemical regeneration), water supply; and effluent treatment. Andritz supplied technology for log receiving, two chipping lines, bark processing, chip storing and reclaiming (shown here), chip screening, and chip conveying to the cooking plant. The total processed wood amount is 4,800,000 m^3 sub per year. The fibreline includes a DownFlow Lo-Solids digester with TurboFeed chip feeding, brownstock washing, screening, postoxygen washing, and bleaching. In total, there are eight DD washers in the fibreline. Daily design capacity is 4,090 admt/day at 92 % ISO brightness. Design capacity of the recovery boiler is 5,710 tds/day at 495 ° C and a pressure of 96.8 bar. The recausticizing plant is designed to product 13,370 m^3/day of white liquor. The Lime Kiln has a capacity of 1,100 tonnes/day of burnt lime. The pulp drying plant consists of two parallel lines including pulp screening/ cleaning, TwinWire pulp machines, airborne sheet dryers, and cutter/layboys. The seven-effect evaporation plant has a capacity of 1,466 tonnes/h. Integrated in the design are systems for stripping and methanol liquefaction, processing of bio-sludge and chlorine dioxide plant brine, and removal of chlorine and potassium from the black liquor. A Duct Stripper is utilized to improve condensate quality. Three automated lines produce baled, wrapped, and palletized units ready for shipment to Montes del Plata's global customers. Andritz was responsible for the automation, electrification, and instrumentation in each process area with the exception of the DCS. Included in the delivery were Advanced Control (ACE) optimization software, web-based training tools for operators and maintenance personnel, and the IDEAS Simulator for DCS checkout and operating "virtual" training. Andritz delivered all the centrifugal process pumps including medium consistency as well as fan pumps.

The mill is proposing to utilize the water resource of the Rio de la Plata for process and cooling. The mill will be supported by its own energy generation plant, which will run on energetic rating of black liqueur and bark recovered from incoming tree trunks and other combustibles produced at the plant. The biomass power plant has a potential to generate 170 MW, 90 MW will be used in the plant and up to 80 MW could be sold to the Uruguayan national grid. The power plant will be located in the plant area and will include the following sub-components: a recovery boiler and a biomass boiler for the production of steam; turbine generator; substations, electrical rooms and interconnection with the national grid; and storage facilities for heavy fuel oil reserves to be used for starting up the mill and for backup purposes.

5.12 Oji Holdings Nantong Pulp Mill Jiangsu Province, China

Oji Holdings has started a 700,000 tonne/year BHK pulp line at Nantong mill Jiangsu Province, in the southern part of China. Metso has supplied a greenfield kraft pulp mill; scope of supply covers all main process equipment for the new mill, including chip screens and storage systems, a continuous cooking system, a fibreline including wash presses, ozone bleaching, a wet lap machine, a recovery boiler, an evaporation system, a white liquor plant and a gas handling system. The state-of-the-art technology delivered by Metso ensures environmentally friendly and efficient production. The mill is beginning trial runs and will make BHK pulp at a rate of 500,000 tonnes/a when commercial production begins (KSH Consulting 2014). The BHK line has a design capacity of 700,000 tonnes/a. More than a half of the output on the line will be integrated with the Nantong mill's sole 400,000 tonne/a coated fine paper machine, PM 1, with some tonnage likely to be shipped to the company's 20,000 tonne/a tissuemill in Suzhou city, also in Jiangsu province. The remaining BHK pulp from the line, amounting to 240,000 tonnes/a, will be sold on the Chinese market. The market pulp will be in slurry form, with a moisture content of 50 %.

5.13 Aracruz's Pulp Line, at Their Guaiba Mill in Rio Grande do Sul, Brazil

Aracruz's has set up new 1.5-million-tonnes/year bleached hardwood kraft (BHK) pulp line, at their Guaiba mill in Rio Grande do Sul, Brazil. The expansion will raise the mill's total annual capacity to almost 2 million tonnes (www.bloomberg.com/apps/news?pid=newsarchive&sid.). The production is expected to start in 2015. Metso will supply the entire fibre line comprising pulp cooking, screening and washing, bleaching, drying and baling, as well as the recovery boiler and white liquor preparation systems. Metso will also provide process control systems, including the necessary analyzers and special equipment for quality and runnability management.

The fibre line process features the latest evolution of cooking and washing technologies. The continuous digester is designed for a daily capacity of 5,030 tonnes. The drying machine will have a trim width of 9.99 m and is designed for 4,970 tonnes daily production. Metso will supply for black liquor burning has a design capacity of 6,130 tonnes dry solids per day. The boiler employs technology to maximize power generation from bioenergy. The nominal capacity of the white liquor plant will be 14,300 m^3 of white liquor per day. Aracruz is the world's leading producer of bleached eucalyptus pulp. Total production today is the equivalent of 3.2 million tonnes a year, produced by three pulp mills: Barra do Riacho (2.3 million tonnes), Guaiba (450,000 tonnes) and Veracel (450,000 tonnes, or 50 % of the unit's total capacity).

5.14 Ilim Group's New Kraft Pulp Mill, in Bratsk, Irkutsk Oblast, Russia

Ilim Group's has started a new kraft pulp mill, in Bratsk, Irkutsk Oblast, Russia. Ilim Group on June 19, 2013 officially inaugurated its new pulp mill at its Bratsk pulp and containerboard mill (Irkutsk Oblast) in Russia. The annual capacity of the new fibreline after ramp-up will reach 720,000 tonnes of bleached softwood market pulp, with the total annual pulp and paper products output of the Bratsk Mill exceeding 1 million tonnes per year www.paperage.com/2013news/06_28_2013ilim_bratsk_pulp_mill.html. Metso's delivery to Ilim Group represents state-of-the-art pulping technology. Metso will supply a complete fibre line comprising a CompactCooking G2 digester, a screen room with DeltaScreen screens, an OxyTrac oxygen delignification system, brown stock washing and bleaching plants with TwinRoll Evolution wash presses and a DryWay drying line with a Fourdrinier wet end and two Robobaling lines. Integral to the Bratsk reconstruction program are a new Metso recovery boiler and an upgrade of the evaporation plant. Metso will also deliver a metsoDNA CR automation system for all process areas, and necessary analyzers and special equipment for quality and runnability management. The new pulp mill will produce 720,000 tonnes of bleached softwood market pulp a year, bringing the overall annual pulp production at Bratsk to over 1 million tonnes. When in operation, the Bratsk mill will be one of the world's largest and most modern softwood pulp production facilities. Ilim Group is a leading Russian pulp and paper producer, headquartered in St. Petersburg. The strategic partner of Ilim Group is International Paper, a global leader in the paper and packaging industry. The total annual pulp and paper production volume of Ilim Group is more than 2.3 million tones.

5.15 Metsa-Botnia, Rauma Mill

Metsa-Botnia, Rauma Mill of Finland came on stream in 1996 as the world's first mill built solely for producing chlorine-free TCF pulp. The Rauma mill changed its bleaching system from TCF to ECF in summer 2007 (www.metsafibre.com/Company/ProductionUnits/Pages/raumamill.aspx). It produces 650,000 tonnes/a of ECF bleached softwood pulp in a single line. Metso supplied wood room with two debarking-chipping line and fibreline and the main machinery for brown stock washing, comprising TwinRoll™ displacement presses. A baling line for this new fibreline was also included in the Metso Paper delivery. The equipment was delivered during 1994–1995 and the start-up of the SuperBatch cooking system took place in January, 1996. The cooking process was updated to SuperBatch-K in September 2000. Metso Paper supplied Metsa-Botnia, Rauma Mill with a wood room to handle abt. 2.5 million solid m^3 softwood annually. The softwood raw material is 20–30 % spruce and the rest is pine. The wood room has two debarking-chipping lines each with a capacity of 350 solid m^3/h. Uniform, high quality chips for Rauma Mill's reinforcement pulp are produced with the following machinery: Two GentleFeed™ log feed systems, 72 m Two EasyTyre™ debarking drums, 5.5 × 35 m Two GentleSlice™ chippers, 0 3.3 m, providing an optimum yield of raw material. The SuperBatch cooking system is designed for 1,700 adt/day production for softwood, mainly domestic pine and spruce as raw material. The design kappa was 18 for softwood pulp. The cooking system comprises ten 400 m^3 digesters made of SS 2273 duplex steel. A 500 m^3 chip silo and all the chip conveying screws from silo to digesters were also included in the delivery. The cooking process was updated to SuperBatch-K in September 2000. Two TwinRoll™ A-1872 displacement presses were installed for brown stock washing. The designed production is 1,700 adt/day bleached softwood pulp. The TwinRoll presses installed are the biggest units in the world. The order also included the main equipment, basic engineering, training and start-up supervision. Metso Paper also supplied two additional presses to Metsa-Botnia, Rauma Mill. The first one, a TwinRoll A-1572 was installed as the first washing stage in the bleaching plant. The second, a TwinRoll W-1255S dewatering press, was installed for the pulp prior to entering the paper mill. Baling systems The Metso Paper baling system comprises two baling lines, known as the domestic line and the export line. The latter also has an additional wrapper storage line. Capacity per line is 250 bales/h.

5.16 Metsa-Botnia Joutseno Mill

The Joutseno mill was completely modernised at the turn of the twenty first century. The Joutseno mill has the capacity to produce 670,000 tonnes per year of ECF bleached softwood pulp (www.metsafibre.com/Company/ProductionUnits/Pages/Joutseno.aspx). The mill is a world leader in efficiency and environmental management and a pioneer in renewable energy utilization. The mill produces more bio energy than it needs. This mill is a carbon neutral pulp mill during normal operation. It specialises in manufacturing pulp for wood-fibre printing papers (SC and LWC) and for high-quality coated printing and speciality papers. Wood consumption is 3.5 million m^3 annually. Metsä Fibre has introduced polysulfide cooking in their Joutseno mill in the year 2013. The technology for the preparation of polysulfide, and the digester modifications to enable production of the improved softwood pulp, were supplied by Andritz. According to Joutseno Mill Manager Risto Joronen, the use of polysulfide cooking liquor enables the mill to improve certain pulp qualities that benefits papermakers. One of those benefits is a reduction in specific energy to refine the pulp, resulting in lower operating costs for papermakers. There are also some enhancements to the fibre bonding due to the retention of certain hemicellulose materials in the pulp. The Joutseno mill is also increasing its fibre yield, which makes the investment economically beneficial. As a result, the mill is able to reduce the loading of its recovery boiler which allows it to improve production capacity. According to Andritz, the polysulfide process modifies conventional white cooking liquor to "orange liquor" (named due to the characteristic colour of the modified liquor) by oxidizing sodium sulfide in the liquor to polysulfide. The plant provided is based on the proven MOXY process (white liquor sulfide-to-polysulfide conversion), already installed in several mills around the world. Andritz also modified Joutseno's cooking plant to optimize the new process.

5.17 Stora Enso's Nymölla Mill

Nymölla Mill – part of the Stora Enso Group's Printing and Reading business area – is a modern pulp and fine papers mill. Annual production capacity is 340,000 metric tonnes of pulp and 470,000 metric tonnes of paper. Nymölla Mill is located on the coast, in Bromölla Municipality, about 20 km east of Kristianstad. The Skräbe River, with excellent fishing waters, flows past the plant area and is the source of the mill's process water (assets.storaenso.com/…/printingandreading/…/Environmental%20stateme). The wood raw material consists of roundwood mostly spruce, pine, beech, aspen and sawmill chips. In the wood room, the wood is debarked and chipped. The bark is collected, dewatered and burned in the boiler house. All the softwood chips are stored for about 6 weeks in chip piles to reduce the pitch content and other extractive matter in the chips through the activity of microorganisms. The chips are transported to the digester after storage. Cooking is done with magnesium bisulfate. Cooking is done in batches. The cooking is done for about 8 h. After that the pulp is screened and washed. The digester liquid known as weak liquor is then separated from the pulp. The recovery process for digester chemicals consists of (1) the evaporation of the weak liquor to thick liquor, (2) combustion of the thick liquor in two recovery boilers and (3) the preparation of new cooking liquor from the recovered chemicals. The recovery rate for digester chemicals is at least 95 %. There is also a solid fuel boiler, in which bark, twigs, screening rejects, fuel chips, ultrafiltration concentrate and sludge from the wastewater treatment plant, and also oil and LPG, are burned. The steam from the boilers is transported to two back-pressure turbines that produce approximately 30 MW of electrical power. The pulp is bleached after screening and washing. Nymölla is not using chlorine-based chemicals for bleaching. It is using oxygen, sodium hydroxide, hydrogen peroxide and peracetic acid as bleaching chemicals, and EDTA is used as a chelating agent. The bleaching process takes about 8–12 h. After bleaching, the pulp is again screened. Following bleaching and screening, the pulp is pumped to the paper mill for production of fine papers. A small portion of the pulp is dried and stored for subsequent use. Fine papers are produced on two paper machines (PM1 and PM2). Softwood and hardwood pulp from the pulp plant are used as the fibre raw material, together with a certain amount of purchased pulp from other pulp plants. The paper machines produce uncoated fine papers in grammages ranging from 70 to 160 g/m^2. The paper is trimmed into rolls or sheets of various sizes, and then packaged. The packaged products are then loaded for transport to the customers. Wastewater is treated first in primary clarifiers and biologically in an activated-sludge plant. A significant portion of the bleach plant wastewater also receives preliminary treatment in an ultrafiltration plant, where substances that are difficult to break down in the activated-sludge plant are separated out. Small molecular size substances pass through the membrane and are transported onward to the external wastewater treatment plant. The larger molecules that remain, are burned in the solid fuel boiler. Small molecular size substances pass through the membrane and are transported onward to the external wastewater treatment plant.

Electrical filters and special flue gas scrubbers are used to clean air flue gases from the boilers primarily to remove sulfur dioxide and dust from the flue gases. Urea is also injected into the boilers to reduce emissions of nitrogen oxides. A portion of the flue gases is transported to a plant for producing filler (precipitated chalk) adjacent to the paper mill and used there as process gas. Gas flows in the pulp plant that contain odorous substances are channeled to one of the boilers, where these odorous substances are burned.

5.18 UPM Fray Bentos Pulp Mill

UPM Fray Bentos pulp mill was started up in November 2007. The Fray Bentos pulp mill is one of the most modern pulp mills in the world. It has a capacity of 1 million tonnes/a of fully bleached eucalyptus market pulp. The entire process and all the areas of the pulp mill have been designed and implemented according to the IPPC BREF to comply the Best Available Techniques for chemical pulp manufacturing. Basically the entire raw material supply of the mill comes from the eucalyptus plantations of Forestal Oriental from usually within the maximum distance of 200 km from the mill. When having reached the full capacity, the mill will use more than 3 million solid cubic meters of eucalyptus, mainly Eucalyptus Grandis. The cooking of eucalyptus is performed using two-vessel downflow Lo-Solids cooking

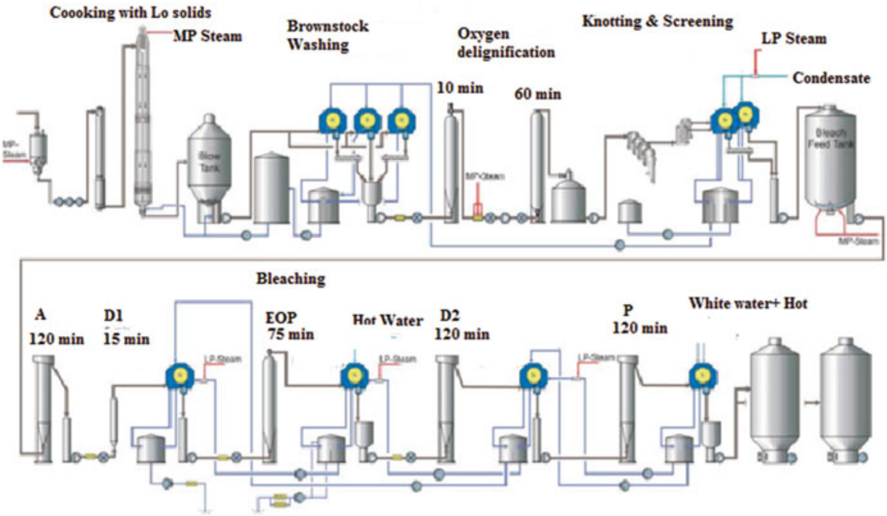

Fig. 5.13 Fray Bentos Pulp mill fibre line (Saarela et al. 2007. Reproduced with permission)

process (Saarela et al. 2007). The pulp is cooked to kappa number 18. The mill is using oxygen delignification which is performed in two stages. The kappa number is brought down to the level of 10. Pulp is then bleached to the full market pulp brightness of 91 % ISO. The bleaching sequence is A/D-EOP-D-P. The black liquor evaporation is performed in seven effects to reach the dissolved solids concentration of 80 %. The recovery boiler has the combustion capacity of 4,450 tonnes solids/day and the steam values are 94 bar (g) and 490 °C. Andritz is the main supplier of the fibreline and recovery island. Figure 5.13 shows the Fray Bentos Pulp mill fibre line.

5.19 New Projects

Several new projects have been announced (Forest Industry News 2014 www.ksh.ca/2014PDF/Forest%20Industry%20News%20Jun%20Jul%20). Few are mentioned below:

Metsä Fibre, part of Metsä Group, is planning to build a next generation bio-product mill in the existing mill area in Äänekoski, Finland (www.metsafibre.com/…/Bio-product%20mill/Bio-product-mill-press-con). When materialized, the approximately EUR 1.1 billion investment would be the largest ever investment in the forest industry in Finland. The new mill with an annual pulp production capacity of 1.3 million tonnes is planned to be operational in 2017. The new mill will be the world’s first next-generation bio-product mill that can convert wood raw material into a diverse range of products. In addition to high-quality pulp, the mill will produce bio-energy and various bio-materials in a resource-efficient way. A unique bio-economy ecosystem of companies will be built around pulp production. This new mill will be the most efficient and modern bio-product mill in the world. The global increase in the demand for high-quality softwood pulp is the most important driver for the investment. The investment will support Metsä Fibre's growth and improve profitability in the long term. The bio-product mill will contribute to achieving renewable energy targets in Finland through increasing the share of renewable energy by approximately two percentage points. Furthermore, the mill will not use any fossil-based fuels; all of the energy required for it will be generated from wood. The wood raw material and side streams will be utilised 100 % as products and bio-energy. The mill will increase the consumption of fibre wood in Finland by approximately 4 million m^3 (some 10 %) per year. The annual harvesting of softwood can be increased sustainably by approximately 7 million m^3, and birch fibre by 4 million m^3. The fibre wood will be procured mainly in Finland. Metsä Fibre will launch the EIA and environmental permit processes immediately with the aim to have them completed during the first quarter of 2015. The final investment decision is planned to be made in early 2015, in which case the new mill would become operational during 2017.

Södra Cell, Sweden is expanding the capacity of their Värö pulp mill (www.paperage.com/…/06_03_2014sodra_varo_pulp_mill_valmet.html). The pulp production capacity will increase from 425,000 tonnes to 700,000 tonnes/year. Valmet has received a major rebuild and new equipment order. Valmet's delivery will contribute to Södra's performance by significantly increasing the Värö mill's pulp production capacity and energy efficiency. The order consists of a new continuous cooking plant and upgrades of wood handling, fibre line, evaporation plant, recovery boiler, recausticizing, flash dryer, pulp dryer and baling. On completion of the project, Värö will be one of the world's largest softwood sulphate pulp mills. The start-up of the renewed pulp mill is scheduled in the third quarter of 2016. A large part of the order will be delivered from Valmet's operations in Sweden: the cooking plant and recausticizing from Karlstad, fibre line, flash dryer and baling from Sundsvall, and evaporation and recovery boiler from Gothenburg. The wood handling and pulp dryer delivery will come from Finland.

Klabin, the largest integrated pulp and paper company in Brazil, has planned a new pulp mill in Ortigueira, Paraná, Brazil. Start-up is scheduled for the first quarter of 2016 (www.forstwirtschaft.com/de/aggregator/sources/). ANDRITZ has received major order. The scope of supply of the Andritz covers the woodyard, the complete fibreline (for softwood and hardwood), and the white liquor plant. The pulp mill will have an annual production capacity of 1.5 million tonnes, 1.1 million tonnes thereof in short fibre and 400,000 tonnes in long fibre. Klabin operates 16 plants (15 in Brazil and one in Argentina), targeting markets such as packaging paper and board, corrugated packaging, and industrial bags producers. The new pulp project in Brazil is the largest investment in Klabin's history and will double the company's production capacities.

OKI Pulp and Paper Mills has planned a pulp mill project in South Sumatra, Indonesia (www.pulpandpaperonline.com/…/valmet-oki-pulp-paper-mills-supplying). Valmet supplies a part of pulp mill equipment and systems with a value of approximately EUR 340 million. The new mill is expected to produce approximately 2 million ADT (air dry tonne) of pulp annually. The commercial production is expected to begin in 2016. Valmet's delivery includes the following parts of the pulp mill: two biomass gasifiers, two biomass boilers, an evaporation system, two lime kilns and two pulp dryers.

References

Alliance for Environmental Technology (AET) (2007) Trends in world bleached chemical pulp production: 1990–2007

Andrede M (2011) The fibre line of the future for eucalyptus kraft pulp, Keynote presentation. In: 5th international colloquium on eucalyptus pulp, Porto Seguro, Brazil, 9–11 May 2011

Andritz (2012) World records after start-up of greenfield pulp mill of Zhanjiang Chenming, China. www.andritz.com/group/gr-news/gr-news-detail.htm?id

Andritz (2014) Greenfield Montes del Plata mill inaugurated in Uruguay. Spectrum – Andritz magazine of Pulp and Paper, Issue 30 – No. 2. spectrum.andritz.com/ru/index/iss_30.htm

Beca AMEC (2004) Independent advice on the development of environmental guidelines for any new bleached eucalypt kraft pulp mill in Tasmania for resource planning and development commission, Tasmania. http://www.rpdc.tas.gov.au/__data/assets/pdf_file/0005/66335/Study_Report.pdf

Beca AMEC (2006) Review of ECF and TCF bleaching processes and specific issues raised in the WWF report on Arauco Valdivia. Prepared for resource planning and development commission. Tasmania, Australia. May 2006

Chandra B (1997) Effluent minimization – a little water goes a long way. Tappi J 80(12):37–42

KSH Consulting (2014) www.ksh.ca/2014PDF/Forest%20Industry%20News%20Jun%20Jul%20

Forest Industry News (2014) www.ksh.ca/2014PDF/Forest%20Industry%20News%20Jun%20Jul%20

Gullichsen J, Fogelholm CJ (2000) Chemical pulping—papermaking science and technology. Book 6A. Fapet Oy, Helsinki, p A19

Hart PW, Rudie AW (2012) The bleaching of pulp, 5th edn. Tappi press, Atlanta

Jiang ZH, Van Lierop B, Berry R (2000) Hexenuronic acid groups in pulping and bleaching chemistry. Tappi J 83(1):167

Johnson T, Santos CA, Herschmiller D, Palmiere M, Trepte R, Purdie D (1996) APP, AlPac and Bahia Sul – current design and environmental performance for ECF in the Americas. In: International pulp bleaching conference, Washington

Johnson AP, Johnson BI, Gleadow P, Silva FA, Aquilar RM, Hsiang CJ, Araneda H (2008) 21st century fibre lines. In: Proceedings of international pulp bleaching conference, Quebec City, p. 1

Johnson T, Johnson B, Gleadow P (2009a) The fibreline of the future, pulp and paper international, PPI magazine, March 2009. www.risiinfo.com/magazines/march/2009/ppi/the-fibreline-of-the-future.html

Johnson T, Johnson B, Gleadow P, Araneda H, Silva F, Aquilar R, Hsiang C (2009b) 21st century fibrelines. Pulp Pap Can 110(9):26–31

Knight P (2002) Aracruz concept pays off. Pulp & Paper International, www.risiinfo.com/magazines/September/2002/PPI/pulp-paper

Lindstrom LA (1990) Oxygen stage design and performance. In: Tappi bleach plant operations short course notes. Tappi Press, Atlanta, p 89

Lindstrom LA (2003) Impact on bleach ability and pulp properties by environmentally friendly bleaching concepts. In: Metso paper pulping technology seminar, Hyderabad, November 2003

McDonough TJ (1996) Oxygen delignification. In: Dence CW, Reeve DW (eds) Pulp bleaching – principles and practice. Tappi Press, Atlanta, p 213

Metso (2005) Zellstoff Stendal. Fiber Pap 7(1):12–17

National Council for Air and Stream Improvement Inc (NCASI) (2003) Pulp mill process closure: a review of global technology developments and mill experiences in the 1990s. Technical Bulletin No. 860. National Council for Air and Stream Improvement, Inc, Research Triangle Park

Nelson PJ (1998) Elemental Chlorine Free (ECF) and Totally Chlorine Free (TCF) bleaching of pulps. In: Young RA, Akhtar M (eds) Environmentally friendly technologies for the pulp and paper industry. Wiley, New York, p 215

Nelson PJ, Chin, CWJ, Grover SG, Ryynänen H (1995) Elemental Chlorine-Free (ECF) and Totally Chlorine-Free (TCF) bleaching of eucalyptus kraft pulps. In: Appita annual general conference proceedings, p 179

Pikka O, Vessala R, Vilpponen A, Dahllof H, Germgard U, Norden S, Bokstrom M, Steffes F, Gullichsen J (2000) Bleaching applications. In: Gullichsen J, Fogelholm C-J (eds) Chemical pulping—papermaking science and technology. Book 6A. Fapet Oy, Helsinki, p A19

PPI mills and technology (2012) ppimagazine.com/mills/asia-pacific/zhanjiang-chenming-sets-record-pulp-production-700000-tyr-andritz-supplied-process-technologies-greenfield-pulp-mill-china

Pryke DC (2003) ECF is on a roll: it dominates world bleached pulp production. Pulp Pap Int 45(8):27–29

Rodden G (2005) Greenfield mill. PPI Magazine (Pulp & Paper International) www.risiinfo.com/db_area/archive/ppi_mag/2005/01/01.html

Rodden G (2006) The birth of a giant. Pulp Pap Int 48(4):13–17

Rodden G (2007) Nueva Aldea starts up smoothly. PPI Magazine (Pulp & Paper International) http://www.risiinfo.com/magazines/February/2007/PPI/4380.html

Saarela S, Garcia E, Eluen I, Fernandez, V (2007) The first year of operation of the Botnia Fray Bentos pulp mill in Uruguay, Ruta Puente Puerto, Botnia

Shaw M (2004) New fibre line offers top-tier quality, environmental performance for bowater. Pulp and Paper magazine www.risiinfo.com/…/New-Fibre-Line-Offers-Top-Tier-Quality-Environ

Toland J (2004) Stendal starts up. Pulp & Paper International, www.risiinfo.com/magazines/December/2004/PPI/Stendal-starts-up

Vuorinen T, Fagerström P, Buchert J, Tenkanen M, Teleman A (1999) Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps. J Pulp Pap Sci 25(5):155–162

Wold D (2008) Nueva Aldea: a gleaming example of a modern pulp mill. Fibre & Paper & Power, www.valmet.com/…nsf/…/Pages4-7from108Fibre&Paper&Power.pdf?

www.aet.org

www.forstwirtschaft.com/de/aggregator/sources/

www.metsafibre.com/…/Bio-product%20mill/Bio-product-mill-press-con

www.metsafibre.com/Company/ProductionUnits/Pages/Joutseno.aspx

www.metsafibre.com/Company/ProductionUnits/Pages/raumamill.aspx

www.paperage.com/…/06_03_2014sodra_varo_pulp_mill_valmet.html

www.paperage.com/2013news/06_28_2013ilim_bratsk_pulp_mill.html

www.pulpandpaperonline.com/…/valmet-oki-pulp-paper-mills-supplying

www.valmet.com/en/products/pulping…/WTB-110628-2256F-F0632

www.valmet.com/valmet/products/…nsf/…/Results313Eldorado.pdf

www.veoliawaterstna.com/news-resources/…/veracelhpdevaporators.htm

Chapter 6
The Future

Abstract Minimum Impact Manufacturing has and will continue to be the vision of the pulp and paper industry. The vision of the forest products industry as an ecocyclic industry is becoming firmly established. This vision is aimed at sustainable development, resource utilization, efficient internal conversion and recycling of fibers, chemicals and energy. The large majority of companies are now taking steps toward implementing ecocyclic processes at their plants. Future technologies may emerge that make additional progress toward the minimum-impact mill. The pace of research and development of new technologies has quickened dramatically in the last decade, giving manufacturers more options to consider. Pulp mills have been identifying new pathways to go beyond the production of pulp and electricity. One widely discussed approach is the integration of multi-products biorefineries, providing an opportunity to contribute to the future demands for energy, fuels and chemicals.

Keywords Pulp and paper industry • Pulp mill • Minimum impact manufacturing • Minimum-impact mill • Sustainable development • Resource utilization • Recycling • Energy • Electricity • Biorefinery • Energy • Fuel • Chemical

The future of the paper industry will be the minimum-impact mill. Closed loop, and minimum impact concepts continue to be intensively researched and implementation of process improvements is ongoing. The vision of the forest products industry as an ecocyclic industry is becoming firmly established in the minds of many people (STFI 2003). This vision involves much more than simple environmental compliance. It is aimed at following (Warnqvist 1999):

- Sustainable development
- Resource utilization
- Efficient internal conversion and recycling of fibers
- Chemicals and energy

At the mill level, ecocyclic principles require closed cycle compatible process technology. But this does not necessarily mean that mills are 'totally effluent-free' or TEF. Instead, the process could be considered as MEM (minimum effluent mill), MIM (minimum impact mill), or even 'minimum input mill' in view of the elemental input/output mass balance equation Sustainable development cannot be achieved without continuous innovation, improvement, and use of clean

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technologies and "green" chemistry to make fundamental process changes to reduce pollution levels and resource consumption. According to Colin L. Powell United States Secretary of State "Sustainable development is a compelling moral and humanitarian issue. But sustainable development is also a security imperative." The large majority of companies are now taking steps toward implementing ecocyclic processes at their plants, but the concept also goes beyond the mill itself (STFI 2003). The idea also encompasses the flow and delivery of recycled resources to other industries, society and markets. In Sweden, the main driving force behind the introduction of MIM or MEM mills comes from the Swedish environmental protection agency, the Naturvårdsverket (Warnqvist 1999). The organization is calling for effluent COD targets of 10–15 kg/ADT. This will typically require a comparatively small total effluent volume at a mill – about 20 m/ADT or less – of which bleach effluent accounts for 5–10 m/ADT. In many cases, the optimum solution in both technical and economic terms would be to combine internal process measures and efficient external treatment. Within the global closed cycle vision, the future of kraft pulp mills is likely to center more and more on the MIM concept. Both meanings – minimum impact mill and minimum input mill – are likely to play an important part in the process. Introducing this new concept will involve challenges for the mill's process technology, management, operation and control. Equally, the MIM concept poses significant challenges on the technical research and development side for both suppliers and consultants in the industry.

Chemical pulping technology has changed and developed rapidly in the past decade. The pressure to develop comes primarily from two directions: concern about the environment, and increased global competitiveness in the pulp and paper business. Environmental organizations throughout the world are educating both consumers and pulp and paper producers to accept the philosophy that no effluents with unknown environmental consequences should be allowed. Meanwhile, global competition has subjected all producers to strong price and quality competition. Therefore, equipment/technology suppliers are continually seeking to improve and optimize the processes and deliveries to obtain the best possible quality and economy for the customers.

Pulp and paper mills have presently the appearance of largest water consumer and biggest polluter because of residual odor and visual aesthetic disturbances from water vapor. Until some of these very real community impacts are taken care of, the industry will continue to have trouble building public credibility in spite of strong technical arguments demonstrating "absence of harm". The vision of minimum-impact manufacturing, be it "a completely ecocyclic system for high quality paper production which efficiently utilizes the energy potential of the biomass" has captured the imaginations of the industry's leaders (Axegard et al. 1997). Opportunity exists to move public view point to "the pulp and paper industry is ecologically sound, while producing recyclable products from renewable resources." However, local issues and other aesthetic issues should be addressed to earn public trust. Efforts should be made to minimize releases from the pulping and recovery processes. Currently there are no “zero” effluent kraft mill bleach plants (NCASI 2003; Stratton et al. 2005).

There has been marked reductions in key pollutants such as sulfur oxides, nitrogen oxides, chlorinated organics, BOD and COD. It is also important to note that the industry’s emissions of carbon dioxide per ton of product has dropped by almost 80–90 % in the developing countries. Ecocyclic visions and sustainable industrial production methods have also become the main focus of the high profile environmental policies formulated by many European and some North American companies. A quick glance at the web sites of these companies confirms this trend.

Mills that recirculate the filtrates from the first bleaching and extraction stages of the bleach plant make additional progress toward the minimum-impact mill. These low-effluent processes represent the most advanced current technologies.

Future technologies may emerge that make additional progress toward the minimum-impact mill. The pace of research and development of new technologies has quickened dramatically in the last five years, giving manufacturers more options to consider. Agenda 2020, a research agenda proposed by the American Forest & Paper Association, provides an indication of the trends in research on future technological advances. Chloride removal technologies are currently undergoing a mill-scale demonstration. Other potential future technologies are being tested at the laboratory and the pilot plant scale. These technologies include novel bleaching agents and other process modifications. These new technologies are in different phases of development, and it is difficult to predict when they will become commercially available. Purchasers should recognize that new technologies in pulp and paper manufacturing do not provide benefits to the environment until they are actually running at a commercial scale. In the paper industry, technologies usually require a minimum of 5–10 years of laboratory and pilot plant testing before they reach mill-scale demonstration. Technologies such as oxygen delignification and ozone bleaching took about 20 years from initial laboratory demonstration to successful commercial application, for example.

Today’s State-of-the-Art mills compared to 1975 use less wood to make a piece of paper; are energy self sufficient and export green power to the grid; use 70 % less water, discharge less solid waste, and emit 96 % less SO_2 and 90 % less odorous compounds; protect the ecosystem with advanced wastewater treatment in discharging 95 % less BOD, 90 % less suspended solids, discharging no POP (Persistent Organic Pollutants), creates high quality recyclable products while providing sustainable value to society (www.aet.org/science_of_ecf/ecf_closed…/metafore_presentation.pdf). Minimum Impact Manufacturing has and will continue to be the vision of the pulp and paper industry (Axegard et al. 1997; Erickson 1995; Broman and Lindberg 1997; Pryke 2008). Pulp mills have been identifying new pathways to go beyond the production of pulp and electricity. One widely discussed approach is the integration of multi-products biorefineries, providing, therefore, an opportunity to contribute to the future demands for energy, fuels and chemicals. The potential is vast, considering that the sector is already engaged with the development of tree seedlings, forest management and transportation of logs to the industrial facilities. In addition, pulp mills have the competence to process wood chips and residues in a very effective way. On the other hand, achieving profitable growth through the introduction of new sellable products might be challenging and has to be carefully evaluated (Bajpai 2012, 2013).

References

Axegard P, Carey J, Folke J, Gleadow P, Gullichsen J, Pryke DC, Reeve DW, Swan B, Uloth V (1997) Minimum-impact mills: issues and challenges. In: Proceedings of the minimum effluent mills symposium. Tappi Press, Atlanta, pp 529–541

Bajpai P (2012) Biotechnology in pulp and paper processing. Springer US New York Inc, 412 pp

Bajpai P (2013) Biorefinery in the pulp and paper industry. Academic/Elsevier Inc, Burlington

Broman PG, Lindberg H (1997) Working toward ecobalance. In: 1997 Tappi minimum effluent mills symposium proceedings. Tappi Press, Atlanta

Erickson D (1995) Closing up the bleach plant: striving for a minimum-impact mill. Tappi/NC State emerging pulping & bleaching technologies workshop, May 1995

National Council for Air and Stream Improvement Inc (NCASI) (2003) Pulp mill process closure: a review of global technology developments and mill experiences in the 1990s. Technical Bulletin No. 860. National Council for Air and Stream Improvement, Inc, Research Triangle Park

Pryke D (2008) Perspectives on the pulp and paper industry. Digital Presentation, 2008

Pryke D The Minimum-impact mill: "State-of-the-Art" manufacturing. AEt alliance for. Environmental Technology. www.aet.org/science_of_ecf/ecf_closed.../metafore_presentation.pdf

Stratton S, Gleadow P, Johnson A (2005) Pulp mill process closure: a review of global technology developments and mill experiences in the 1990s. Water Sci Technol 50(3):183–194

Swedish Pulp and Paper Research Institute (STFI) (2003) Ecocyclic pulp mill – "KAM" – final report 1996–2002. KAM Report A100. Swedish Pulp and Paper Research Institute, Stockholm

Warnqvist B (1999) Closing in on the bleached kraft pulp mills. Pulp Paper International. www.risiinfo.com/magazines/october/1999/ppi/pulp-paper/magazine/international/october/1999/closing-in-on-the-bleached-kraft-pulp-mills.html

Index

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