BEST AVAILABLE TECHNIQUES GUIDANCE DOCUMENT ON PULP AND PAPER INDUSTRY

FOREWORD

Best Available Techniques Economically Achievable (BAT) document had been prepared as a guidance notes for the nine (9) major industries in Malaysia and to support the implementation of the new Environmental Quality (Clean Air) Regulations 20xx. These documents were prepared based on the latest state-of-the-art technologies, internationally accepted limit values but had been adjusted and tailored to local requirements.

BAT is defined as the effective methods in preventing pollution and, where generally that is not practicable, to reduce emissions from industrial activities and their impact on the environment. This definition implies that BAT not only covers the technology used but also the way in which the installation is operated, to ensure a high level of environmental protection. Implementations of BAT in any specific industrial sectors are under economically and technically viable condition.

It is hope that the technical contents of these documents will prove beneficial to the industries in their endeavour to comply with the environmental regulations and standards through more cost-efficient means. In the identification of BAT, emphasis is placed on pollution prevention techniques rather than end-of-pipe treatment. These documents will be reviewed and updated from time to time.

These documents have been prepared in consultations with the University of Malaya Consultancy Unit (UPUM), Malaysia German Technical Cooperation (GTZ) and the relevant industries/stakeholders. The Department of Environment wishes to record appreciation to representatives of the relevant industrial sectors, government agencies and individuals for their invaluable input.

DATO' HALIMAH HASSAN
Director General
Department the Environment, Malaysia

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LIST OF ABBREVIATIONS

ADP - Air-dried Pulp
BAT - Best Available Techniques economically achievable
BFBC - Bubbling Fludised Bed Combustion
BKME - Bleached Kraft Mills Effluent
BREF - Best Available Technique Reference Document
CAR - Clean Air Regulation
Cd - Cadmium
CO - Carbon Monoxide
CTMP - Chemithermo Mechanical Pulping
DOE - Department of Environment
DS - dry-solids
ECF - Elemental Chlorine –free
ESP - Electrostatic Precipitators
FBC - Fludised Bed Combustion
HCl - Hydrogen Chloride
HF - Hydrogen Flouride
IPPC - Integrated Pollution Prevention Control
kg/h - kilogram per hour
mg/Nm^3 - milligram per cubic metre at standard temperature (273K) and pressure (1atm)
MNI - Malaysian Newprint Industry
N_2O - Nitrous Oxide
NCG - Non-Condensable Gases
NMVOCs - Non Methane Volatile Organic Compounds
NO_x - Nitrogen Oxide
SFI - Sabah Forest Industry
SNCR - Selective Non-Catalytic Reduction
SO_x - Sulphur Oxide
TCF - Totally Chlorine Free
TOC - Total Organic Compound

tpd	-	tonnes per day
TRS	-	Total Reduced Sulphur
VOCs	-	Volatile Organic Compounds

1.0 PREFACE

1.1 Status of This Document

This document forms a part of a series presenting the guidance notes for selected industries in Malaysia (list given at the end of this preface) to apply best available techniques economically achievable (BAT), associated monitoring and developments in them. This series is published by the Department of Environment (DOE) in accordance to the Environmental Quality (Clean Air) Regulations 2014 (CAR 2014).

1.1 Definition of BAT

In order for the user of this document to understand the legal context of this document, the interpretation on the definition of BAT is taken from Regulation 2 – Interpretation of CAR 2014 and described as below:

“Best Available Techniques Economically Achievable” means the effective methods in preventing pollution and, where that is not practicable, generally to reduce emissions in the air from the industrial activities and their impact on the environment as a whole. In this regard:

“Techniques” includes both the technology used and the way in which the facility is designed, built, maintained, operated and decommissioned;

“Available Techniques” means those techniques that are accessible to the occupier and that are developed on a scale that allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages; and

“Best” means effective in achieving a high general level of protection of the environment as a whole;

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this document that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood to mean those levels representing the environmental performance that could be expected as a result of the application, of the techniques described, taking into account the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such.

In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

The actual cost of applying a technique will depend strongly on the specific situation such as taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific economic viability of techniques drawn from observations on existing installations.

The purpose of CAR 2014 is to achieve prevention and control of pollution arising from activities listed in its First Schedule and Second Schedule. More specifically, it provides for a notification system for certain categories of industrial installations to conduct an integrated and comprehensive view of the pollution and consumption potential of their installation. The overall aim is to ensure a high level of protection of the environment as a whole based on appropriate preventative measures through the application of BAT.

1.2 Objective of This Document

The ‘emission minimization principle’ as cited in CAR 2014 requires that the goal of emission abatement is to achieve minimum emissions as a result of applying current BAT. Hence this guideline document is meant to provide the reference information for the permitting authorities to take into account when determining permit conditions. This document should serve as valuable input to achieve better environmental performance.

1.3 Information Sources

The information is mainly based on the European IPPC BREF document where the assessment was achieved through an iterative process involving the following steps:

- identification of the key environmental issues for the sector
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in Implementation of these techniques;

- selection of the BAT and the associate emission and/or consumption levels for this sector

1.5 How to Use This Document

It is intended that the general BAT in this document could be used to judge the current performance of an existing installation or to judge a proposal for a new installation and thereby assist in the determination of appropriate BAT based conditions for that installation. It is foreseen that new installations could be designed to perform at or even better than the general BAT levels presented here. It is also considered that many existing installations could reasonably be expected, over time, to move towards the general "BAT" levels or perform better. This reference document does not set legally binding standards, but they are meant to give information for the guidance of industry, the relevant government bodies and the public on achievable emission and consumption levels when using specified techniques.

The structure of the guideline document is as follows:

An overview of each particular sector in the Malaysian context is firstly covered briefly followed by process description, process optimization, sources of pollution, emission control options, recommended practices and emission values and finally emission monitoring and reporting. More often than not, trade-off judgements between different types of environmental impacts and specific site condition are the influencing factors.

Another important point to note is that BAT change over time and this guidance document needs to be reviewed and updated as appropriate.

2.0 OVERVIEW

Currently there are only five Malaysian paper mills with annual production capacity of more than 100,000 metric ton. Smaller paper mills have cumulative annual production rate of 310,400 metric tones. Together, Malaysian paper mills produces 65% of Malaysian demand for paper and paperboard if all the mills are producing at full capacity.

Table 1 summarizes the production capacity of major Malaysian Paper Mills based on Malaysian **Pulp and Paper Manufacturers Association 2002 statistics**.

Table 1: Production Capacity of Major Malaysian Paper Mills

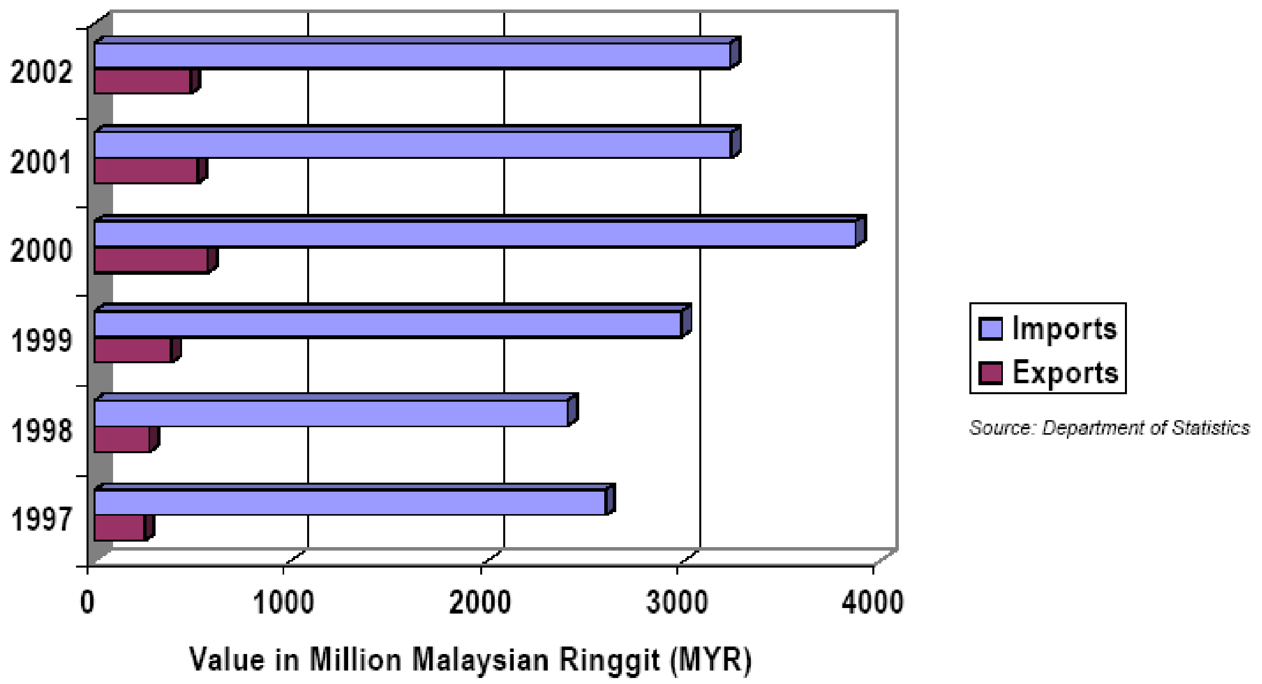
Company Name	Annual capacity, metric ton	Paper types
Genting Sanyen	300,000	Kraft, corrugated
Muda Paper	300,000	Kraft, corrugated
Malaysia Newprint Industry (MNI)	250,000	Newsprint
Sabah Forest Industry (SFI)	165,000	Writing/printing
Pascorp Paper	140,000	Kraft, corrugated
Others below 100,000 metric tonnes	310,400	Various
Total Production In Malaysia	1,465,400	

Kraft and corrugated paper are the main paper types produced. There is only one Malaysian paper mill (MNI) that produces newsprint paper. Similarly, Sabah Forest Industries (SFI) is the only major producer of paper for writing and printing.

Moreover, SFI is the only pulp mill in Malaysia. SFI produces mixed tropical hardwood pulp for their own consumption from wood supply in the adjoining forests. SFI import 5 to 10% of soft wood pulp to supplement their hard wood pulp in the production of writing and printing paper.

Other Malaysian paper mills import unbleached Kraft pulp to mix with waste paper to obtain better tensile strength in their paper products. Waste paper constitutes 95% of raw material in Malaysian paper mills.

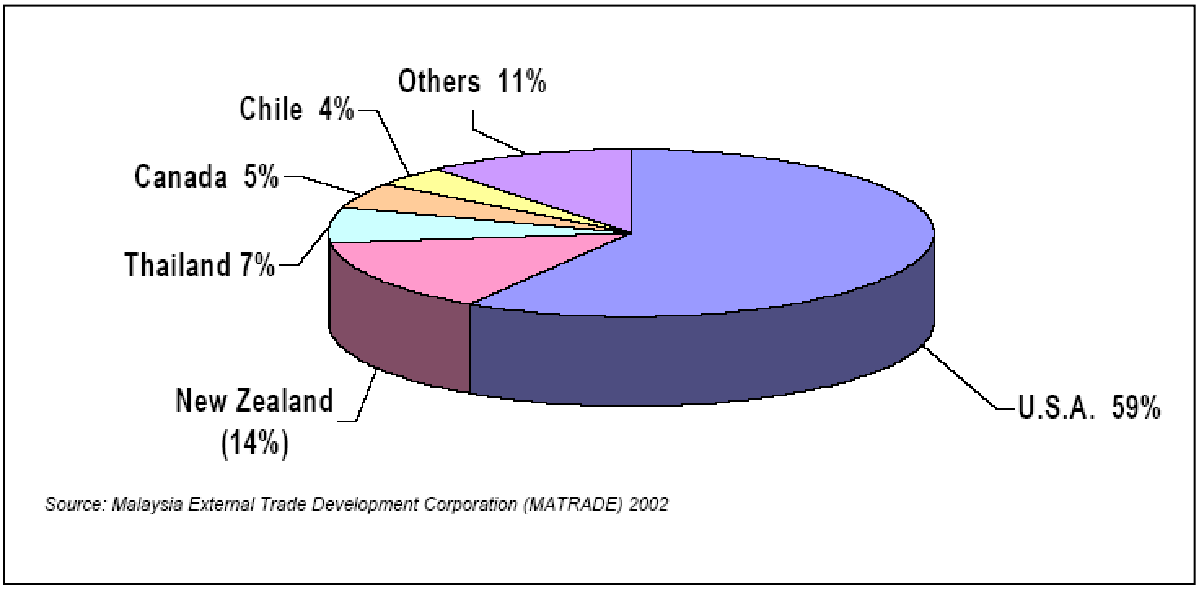
Total imports of wood pulp in 2002 are about RM140 million with a growth of more than 5% compare to 2001**. Figure 1** shows the import and export of pulp and paper from 1997 to 2002. Indicatively, imports exceed exports by 7 times in value in 2002.



Source: Department of Statistics

Figure 1: Import and Export of Pulp and Paper (1997 – 2002)

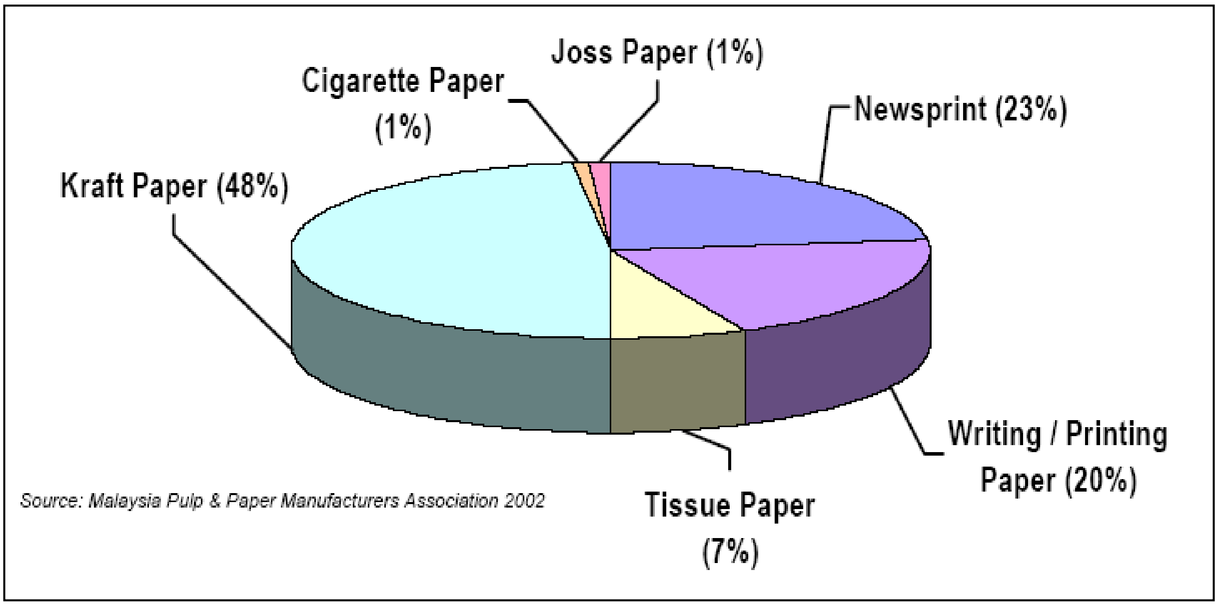
Similarly, United States Of America is the main source of imported wood pulp as shown in **Figure 2**



Source: Malaysian External Trade Development Cooperation (MATRADE) 2002

Figure 2: Source of Wood Pulp from Five Countries by Imports

Paper consumption in Malaysia ranges from cigarette paper, joss paper, Kraft paper, newsprint, tissue paper and writing/printing paper (**Figure 3**) However, Kraft paper registers the highest consumption out of a total consumption of two (2) million metric tonnes.



Sources: Malaysia Pulp & Paper Manufacturers Association 2002

Figure 3: Consumption of Paper in Malaysia

3.0 PROCESS DESCRIPTIONS

Pulp and paper are manufactured from raw materials containing cellulose fibres, wood, recycled paper, and agricultural residues. This document will focus on Kraft process (dominant process in Malaysia) with unit production capacities greater than 10 metric ton per day (tpd).

3.1 Kraft Process

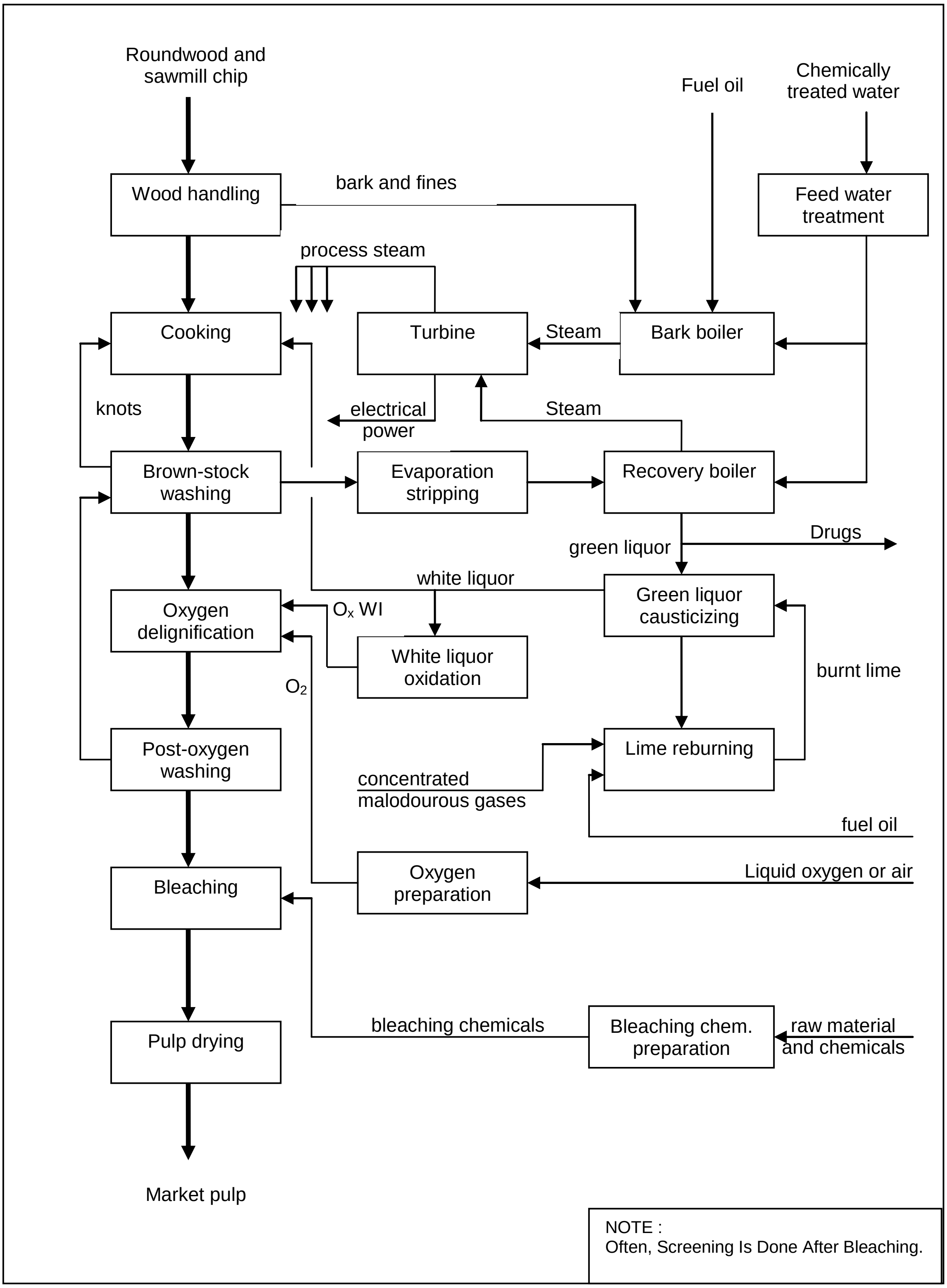
A Kraft pulp mill can be divided into four main parts: raw material handling, cooking and delignification (with almost completely closed chemical and energy recovery system), bleaching (with an open water system) and the process external wastewater treatment system.

Another more conventional division is the fibre line, recovery system and external wastewater treatment. Some auxiliary systems like reject handling, manufacturing of bleaching chemicals and auxiliary power generation are connected to the main departments.

Figure 4 gives an overview of the process of a kraft mill.

3.1.1 Reception and Storage of Wood

Wood may be received as logs directly from the forest or as by-product chips from some other wood working industry like sawmills and plywood mills. Logs are mainly delivered with the bark on and have to be debarked before further processing. Chips are normally free of bark and can be used after screening and possibly washing. The wood is transported to the mills by ship, truck or rail but also to a limited extent by floating logs to the mill site. Where the latter is used, there will be some leaching of resin acids and nutrients while the wood is in contact with water.



NOTE :
Often, Screening Is Done After Bleaching.

Figure 4: Process Overview of a Kraft Pulp Mill [SEPA-Report 4713-2, 1997].

Mechanical pulping techniques may use either logs or chips but chemical pulping techniques will always use chips. The objective in chipping is to form uniform sized chips, which will result in a better pulp product.

Some chemical pulp mills store wood chips in piles for up to 40 days during which time there is some degradation of extractives within the wood by oxidative and enzymatic mechanisms. The pile of wood chips can become quite warm during this maturation period. Storage for greater than 40 days would be expected to reduce the subsequent fibre yield. Mechanical pulping on the other hand requires fresh wood and in all cases it is desirable to maintain the moisture content of the wood.

3.1.2 Debarking

The most common method for debarking is drummed debarking. Bark is removed as the logs rub against each other when made to tumble by the rotating action of the debarking drum. Loose bark and wood sticks fall from the drum through special chutes. Debarked logs are showered with water before being delivered to the pulp mill.

The wet debarking process uses large volumes of water. In recent years “dry” debarking has been installed in many mills. Dry debarking give bark with lower water content, which will result in a better energy balance for the mill if the bark is burnt.

Bark from the debarking unit is typically fed into a bark shredder and, if wet, pressed for burning. Some alternative uses for the bark exist and in some cases it is sold off site but the sheer volume involved in large installations favors on site disposal and energy recovery.

3.1.3 Wood Chipping and Screening

For chemical pulping processes the logs are reduced to chips in a chipper. A uniform chip-size distribution is necessary for the efficiency of the processes and for the quality of the pulp. The more uniform the chips are after the chipper, the lower the raw material consumption. After the chipper station the chips are screened in order to remove oversized chips and sawdust. However, sawdust can also be cooked together with chips or separately in a sawdust cooker, or it can be burnt or used for other purposes. Oversized chips may go for re-processing in a crusher or rechipper. Chips are screened for thickness, as this is a critical parameter both in chemical and mechanical pulping. Often the overall optimum is 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 can be sold for other purposes or burnt in a solid fuel boiler with the heat recovery.

3.1.4 Cooking and Delignification

In the Kraft process the fibres are liberated in the cooking plant by dissolving the lignin and part of the hemicellulose in the cooking chemical solution (white liquor), which contains sodium hydroxide and sodium sulphide as active chemicals. When the final product is unbleached pulp, the cooking is the only delignification stage.

The cooking process can be performed either in batch digesters or in a continuous digester. When using batch processes, in the cooking stage the wood chips and the liquors are charged into a batch digester where the cook is carried out in elevated temperature and pressure. When the desired residual lignin content (measured as Kappa number) is reached, the contents are discharged to a blow tank and the cooking cycle is repeated. The amount of lignin that remains in the pulp can be determined approximately by multiplying the kappa number by the factor 0.165 i.e. a kappa number of 30 relates to about 4.95% residual lignin.

The cooking can also be carried out in a continuous digester where the wood/chemical charge and retention time as well as the temperature in the cooking zone defines the resulting lignin content. The chips are pre-heated by steam before entering the continuous digester in order to remove air, which interferes with the impregnation. After entering the digester, the chips are impregnated with cooking liquor and the temperature raised to 155 - 175°C. The cooking time at the maximum temperature is in the range of 1-2 h. In conventional cooking the delignification of softwood (spruce or pine) can be brought down to a Kappa number of 30 - 35 whilst maintaining acceptable pulp strength properties. For hardwood (aspen, birch and eucalyptus) the Kappa number can be brought down to 14 - 22 [CEPI, 1997].

As a result of the poor bleachability of kraft pulps and the pollution caused by pulp bleaching, several cooking modification methods have been developed with the aim of removing more lignin from the wood during cooking without reducing the yield. The Kappa number from the cooking of softwood can be reduced to a level of 15 - 25 through extended delignification [Finnish BAT report, 1996], while the yield and strength properties are still maintained. This means that 25 - 50% less lignin is left in the pulp compared with pulp that has a kappa of 32. The requirements for any subsequent bleaching chemicals are, therefore, reduced and the effluent discharges from the bleaching plant are decreased. Comparable kappa reductions can be achieved in the cooking of hardwood.

3.1.5 Washing and Screening

The pulp coming from the digester contains both fibres and spent cooking liquor (black liquor). About half of the wood is dissolved in the cooking. Consequently the black liquor contains inorganic chemicals and a large amount of organic substances. The black liquor is removed from the pulp in the subsequent washing and led to the chemical recovery system, where cooking chemicals and energy are recovered.

The dissolved organic substances together with the spent cooking chemicals are washed away from the cellulose fibres in the brown stock washing stages. Modern systems normally recover at least 99% of the chemicals applied in the digester. Washing the pulp coming from a conventional batch digester plant is normally carried out with drum washers, while a continuous digester plant utilises the Hi-heat wash zone in the digester with additional drum washers or diffuser washers. In today's batch as well as continuous cooking fibrelines, washing starts already in the digester by displacing hot black liquor with cold wash liquor. Subsequent washing is carried out in various types of washing equipment, e.g. vacuum drum washers, wash presses, diffusers or wire type washers.

Efficient washing reduces the carry-over of black liquor with the pulp resulting in a decreased consumption of chemicals in bleaching and reduced discharges from the bleaching plant. Efficient washing reduces chemical consumption also in oxygen delignification. The outcome of the washing is highly dependent on the efficiency of the equipment used, the outlet consistency of the pulp and the amount of wash water applied. However, if washing is improved by increasing the amount of wash water, the demand for steam will increase in the subsequent stage to evaporate and concentrate the black liquor.

Wash presses and diffuser washers are especially effective in the removal of dissolved organic substances, and this is one reason why wash presses have become more common, especially as the last washing stage before bleaching. Washing with the longest delay can be achieved in a diffuser type of equipment. Adding carbon dioxide to the wash water will improve the washing effect.

Before further processing, the pulp is screened with pressure screens and centricleaners. The objective of screening is to separate knots and fibre bundles from the main pulp stream with a series of vibrating equipment, filtration through pressure screens and centrifugal separation of fibres and other particles with different specific weights. Rejects from screening constitute a further waste stream to be dealt with.

3.1.6 Oxygen Delignification

After cooking, delignification can be continued by oxygen in one-stage or in two stages with or without intermediate washing. Oxygen delignification can be combined with conventional and extended cooking.

Oxygen delignification takes place in alkaline conditions. In order to maintain the sodium balance of the mill, the oxygen stage normally uses the oxydised white liquor, where sodium hydroxide is the main alkaline chemical and sodium sulphide has been oxidised to thiosulphate. Due to relatively low solubility of oxygen to the alkaline liquor, the delignification reactor is pressurised and the temperature is elevated to about 100 ºC. In oxygen delignification magnesium salt ($MgSO_4$) is added in order to preserve the strength of the pulp. The oxygen is mainly purchased but also some on-site plants are in operation. Because of better selectivity and lower investment costs the Medium Consistency (MC, 10-15%) system has dominated mill installations for the past ten years but high consistency installations (HC, 25-30%) are in use as well. Recently the industry has opted to install two-stage oxygen delignification systems to increase the selectivity of the treatment. Oxygen delignification is usually an intermediate stage in the pulp washing. The wash water is added onto the last washing stage after oxygen delignification and led counter-current to the pulp flow. Washing after oxygen delignification is usually done with one or two wash presses alone or in combination with some other type of washer. The organic material that is dissolved during oxygen delignification can be recovered and led to the chemical recovery system without major changes in the process. The recovery reduces the amount of organic material ending up in the wastewater and the amount of chemicals needed.

The degree of further delignification is 40-50% in a one-stage system and can be up to 70% in a two-stage system [Finnish BAT report, 1996]. The Kappa number after conventional cooking and oxygen delignification is typically 18-22 for softwood and 13-15 for hardwood without extended delignification (CEPI, 1996). Depending on the wood species, oxygen delignification with extended cooking can achieve a reduction in Kappa number to around 8 - 12. The overall pulp yield might decrease by 1.5 - 2.5% and there is still lignin left that has to be removed by other means when high brightness pulp is demanded. The table below summarises kappa numbers currently achieved with different delignification technologies.

Table 2: Kappa Numbers Currently Achieved After Different Technologies Used

Delignification Technology	Hardwood	Softwood
Conventional Cooking	14 - 22	30 - 35
Conventional Cooking and Oxygen Delignification	13 - 15	18 - 22
Extended Cooking	14 - 16	18 - 22
Extended Cooking and Oxygen Delignification	8 -10	8 - 12

The reduction of the Kappa of unbleached pulp (brown stock), whether it is achieved through extended digester delignification, oxygen delignification or some other method, will reduce the load of bleaching-plant pollutants that enter the external effluent treatment system. This is because dissolved substances are piped to the recovery system and then burned in the recovery boiler.

3.1.7 Bleaching

The purpose of bleaching chemical pulp is to obtain certain pulp quality criteria with respect to brightness, brightness stability, cleanness and strength. The brightness of unbleached Kraft pulp is rather low, below 30% ISO whereas fully bleached pulp has a brightness of 88% ISO or higher. Cooking and oxygen delignification cannot remove all the lignin and to achieve this brightness it is necessary to remove or oxidise the remaining lignin and impurities in the pulp. The Kappa number after bleaching is reduced below 1 unit [CEPI, 1996].

Whereas delignification can be carried out within closed water systems bleach plants tend to discharge effluent to external treatment. These effluents from the bleach plant cannot easily be recirculated into the chemicals recovery mainly due to the fact, that these bleach plant effluents would increase built-up of chlorides and other unwanted inorganic elements to the chemical recovery system which can cause corrosion, scaling and other problems. Nevertheless, there are running projects on how to close up the bleach plant and some plants are operated with semiclosed water systems.

The bleaching of kraft pulp is carried out in several stages, usually four to five. The most commonly used chemicals are chlorine dioxide, oxygen, ozone and peroxide. Lately, peracetic acid has become commercially available as bleaching chemical. Chlorine and hypochlorite have largely been phased out as primary bleaching chemicals over recent years (e.g. PARCOM Decision on the Phasing-Out of the Use of Molecular Chlorine (Cl_2) in the Bleaching of Kraft and Sulphite Pulp). Small amounts of chlorine are formed as a by-product in most of the chlorine dioxide generation systems used, and a part of this chlorine will be present when chlorine dioxide is used in bleaching. Chlorine dioxide and ozone have to be produced on site (see Section 4.3.1 and 4.3.2). Peroxide, oxygen and alkali can be delivered to the mills. Ozone is a very reactive bleaching agent whilst chlorine dioxide, oxygen and hydrogen peroxide are less reactive. Because of the different reaction mechanisms different types of bleaching chemicals are utilised in a bleaching sequence. Acid and alkaline stages are used to complement each other.

Peroxide bleaching is relatively slow and requires long reaction times and therefore large reactor volumes or increased pulp consistency. Increased pressure makes higher reaction temperatures possible, resulting in a reduced reaction time or improved bleaching outcome. It is necessary to remove metal ions to avoid degradation of the hydrogen peroxide by using metal chelating agents (i.e. EDTA or DTPA) or acid washing. An advantage with peroxide compared with the other oxygen bleaching chemicals is that peroxide bleaching at optimal conditions brightens the residual lignin.

Enzyme treatment before bleaching has been in use at some plants since 1991. It can be combined with different bleaching sequences to enhance the effectiveness of the chemicals used but typically results in a small loss of yield.

A bleach plant consists of a sequence of separate bleaching stages with different chemicals added. Each bleaching stage consists of:

- devices for mixing the chemicals and the pulp
- a bleaching reactor (up flow or down flow towers) designed with a suitable residence time for chemical reactions
- washing equipment for separation of used chemicals, removed lignin and other dissolved material from the pulp (drum washer or diffuser washer)

The bleaching stages are designed using symbolic shorthand according to the bleaching agent applied:

SYMBOL	**BLEACHING AGENT**
Q	Acid stage where chelating agent EDTA or DTPA has been used for removal of metals
Z	Ozone using gaseous ozone (O_3)
P	Alkaline stage with hydrogen peroxide (H_2O_2) as liquid
D	Chlorine dioxide stage using a water solution of chlorine dioxide (ClO_2)
E	Extraction stage using sodium hydroxide (NaOH)
E/O	Extraction stage using sodium hydroxide with subsequent addition of gaseous oxygen as a reinforcing agent

E/P	Extraction stage using sodium hydroxide with subsequent addition of hydrogen peroxide solution as a reinforcing agent

Nowadays an oxygen delignification has become more and more common delignification stage followed by bleaching sequence of D-E-D-E-D, D-E-D-D, D-EOP-D-E-D or QP-DQ-PO.

Some mills have responded to the market demands of Totally Chlorine Free (TCF) pulps by modifying the bleaching sequence. Nowadays, TCF is an established technology. A number of mills have the possibility of producing ECF- of TCF-pulps depending on the market situation. New sequences have been and are being developed, such as Q-E/P-E-P, Q-Z-P-E-P, OP-ZQ-PO or OPQ-PO [CEPI, 1997].

The introduction of extended cooking and oxygen delignification have resulted to more efficient recovery of organic substances. Thus offering the flexibility of using other chemicals in bleaching and minimisation of use of chlorine chemicals. As a consequence, the total amount of organic compounds and total amount of chlorinated organic compounds have been reduced significantly.

The two main types of bleaching methods in use are so-called ECF (Elemental Chlorine Free i.e. when no molecular or gaseous chlorine is dosed in the bleaching) and TCF (Totally Chlorine Free) bleaching. ECF bleaching uses chlorine dioxide, alkali for the extraction of dissolved lignin, peroxide and oxygen for the reinforcement of the extraction stages. TCF bleaching uses oxygen, ozone or peracetic acid and peroxide with alkali for lignin extraction. Selectivity is important as far as the total yield and pulp quality is concerned because high selectivity means that the bleaching chemical is primarily reacting with the lignin. Chlorine dioxide and chlorine are the most selective bleaching agents and selectivity is better in the bleaching stage than in cooking and oxygen delignification.

TCF bleaching requires a low incoming Kappa for the pulp (10 - 12) to attain full brightness and good strength properties because of the power of the bleaching chemicals and fibre degradation during bleaching although a final brightness of 89% ISO is achievable with TCF bleaching without yield loss. A larger amount of residual lignin remains in TCF bleached pulp than in ECF bleached pulp and this residue has to be stabilised to minimise yellowing after production. ECF bleaching can be done on a pulp with a higher Kappa.

3.1.7.1 Elemental Chlorine Free (ECF) versus Totally Chlorine Free (TCF) Bleaching

Over the last 10 years there were an intensive discussion and research on the environmental benefit of TCF compared to ECF. The evaluation of results of research and of synthesises of the great amount of laboratory and model ecosystem tests as well as field studies with whole mill effluents from bleached kraft mills (BKME) can be summarised as follows:

- The chemical composition of the effluent from modern kraft mills using low-kappa ECF or TCF bleaching of oxygen-delignified low-kappa pulp has largely changed in comparison with the situation 10-15 years ago, even if the operational standard of the individual mills is of major importance for the amount and quality of emissions [SEPA Report 4785, 1997]
- Modern mills with low-kappa ECF bleaching give very low emissions of chlorinated organic substances and high-chlorinated phenolic compounds generally cannot be detected in the effluent [ibid.]
- A comparison of toxic responses of bleach plant and whole mill effluents from mills using different schemes for non-chlorine bleaching, i.e. low-kappa ECF versus TCF bleaching, shows that neither technical concept invariably produces effluents with a lower toxic potency [FEI, 1996]. No clear difference in the effect pattern and effect intensity between effluent from mills using low-kappa ECF (chlorate reduced) and TCF bleaching has been detected.

- Relative merits of low-kappa ECF versus TCF (or vice versa) are not consistent due to different experimental strategies in test procedures and also to non-bleaching factors within the different mills as e.g. the operational standard of the mill [ibid.]
- Secondary treatment of effluents usually tends to decrease the toxicity of the effluents and according to model ecosystem studies effects on ecosystem level are mitigated after external treatment [ibid.]
- Recent model ecosystem studies have indicated a correlation between effluent COD and the effects observed. These findings suggest that it is not a question of whether to use ECF or TCF as the choice of bleaching, but rather to improve the pulping operation in itself [ibid.]. Thus, the amounts of fatty acids, resin acids and sterols in effluent from modern kraft mills are affected more by the fibre raw material or by contributions from the unbleached side rather than from the bleaching process [SEPA Report 4785, 1997]
- A TCF bleaching sequence is the more advantageous alternative for further system closure. However, the use of totally chlorine-free bleaching chemicals requires an extensive removal of the metals (such as manganese, iron, copper ions) out of the pulp due to their negative impact on the peroxide bleaching. This removal is usually effected by a chelating treatment or an acid wash of the pulps.

3.1.8 Bleached Stock Screening

After bleaching there is generally a final screening of pulp. Secondary screening takes place with the same type of equipment than the screening of unbleached pulp.

3.1.9 Drying

In an integrated pulp and paper mill, the pulp stock will be transferred forward to papermaking in a wet state (at about 4% consistency) and the accompanying water forms part of the overall water balance of the mill. For a non-integrated pulp mill where the pulp is not used for manufacturing of paper at the same mill site the pulp will be first pressed and then dried for transport. Drying machine consists of a wire part similar but simpler than wire part of a paper machine for initial dewatering of the pulp. After dewatering stage the pulp is dried with steam in a multi-stage drying part of the machine. After cutting into sheets bales for shipment are formed.

4.0 PROCESS OPTIMISATION

4.1 BAT for Kraft Pulp and Paper Mills

Below, the techniques or combination of techniques that are considered as BAT for integrated and non-integrated kraft pulp mills are given. The following list of BAT is not considered exhaustive and any other technique or combination of techniques achieving the same (or better) performance can also be considered; such techniques may be under development or an emerging technique or already available but not described in this document.

4.1.1 General Measures

1. Training, education and motivation of staff and operators. Pulp and paper mills are operated by people. Therefore, training of staff can be a very cost-effective way of reducing discharges of harmful substances.
2. Process control optimisation. To be able to reduce different pollutants simultaneously and to maintain low emissions, improved process control is required.
3. To maintain the efficiency of the technical units of pulp mills and the associated abatement techniques at a high level, sufficient maintenance has to be ensured.
4. Environmental management system which clearly defines the responsibilities for environmentally relevant aspects in a mill. It raises

awareness and includes goals and measures, process and job instructions, check lists and other relevant documentation.

4.1.2 Measures for Reducing of Emissions to Water

1. Dry debarking of wood
2. Modified cooking either in batch or continuous system
3. Highly efficient brown stock washing and closed cycle brown stock screening
4. Oxygen delignification
5. ECF or TCF final bleaching and some, mainly alkaline, process water recycling in the bleach plant
6. Purification and reuse of condensates
7. Effective spill monitoring, containment, and recovery system
8. Sufficient black liquor evaporation plant and recovery boiler to cope with the additional liquor and dry solids loads due to collection of spills, bleach plant effluents etc.
9. Collection and reuse of clean cooling waters
10. Provision of sufficiently large buffer tanks for storage of spilled cooking and recovery liquors and dirty condensates to prevent sudden peaks of loading and occasional upsets in the external effluent treatment plant
11. Primary treatment of wastewater
12. External biological wastewater treatment

The efficiency of each of these measures varies considerably with the design and operation practices at different mills. To be regarded as a BAT measure it must also be well designed and operated. A combination of the techniques of item 1 to 10 including the general measures results in a range of emissions.

4.2 Chemical and Energy Recovery System for Kraft Pulp Mill

The recovery system in a kraft pulp mill has three functions:

- the recovery of the inorganic pulping chemicals
- the destruction of the dissolved organic material and recovery of the energy content as process steam and electrical power
- the recovery of valuable organic by-products (e.g. tall oil).

The fuel value of the recoverable black liquor is normally enough to make the kraft pulp mills more than self-sufficient in heat and electrical energy. Organic by-products play a limited economic role in most kraft pulp mills.

The main process units in the chemical recovery system are the evaporation of the black liquor (cooking liquor and counter current washing liquor), incineration of the evaporated liquors in a recovery boiler and causticizing, including lime regeneration.

An overview of the circuits of chemicals is presented in **Figure 5** [BMU Austria, 1995] illustrating the main process steps and their functions.

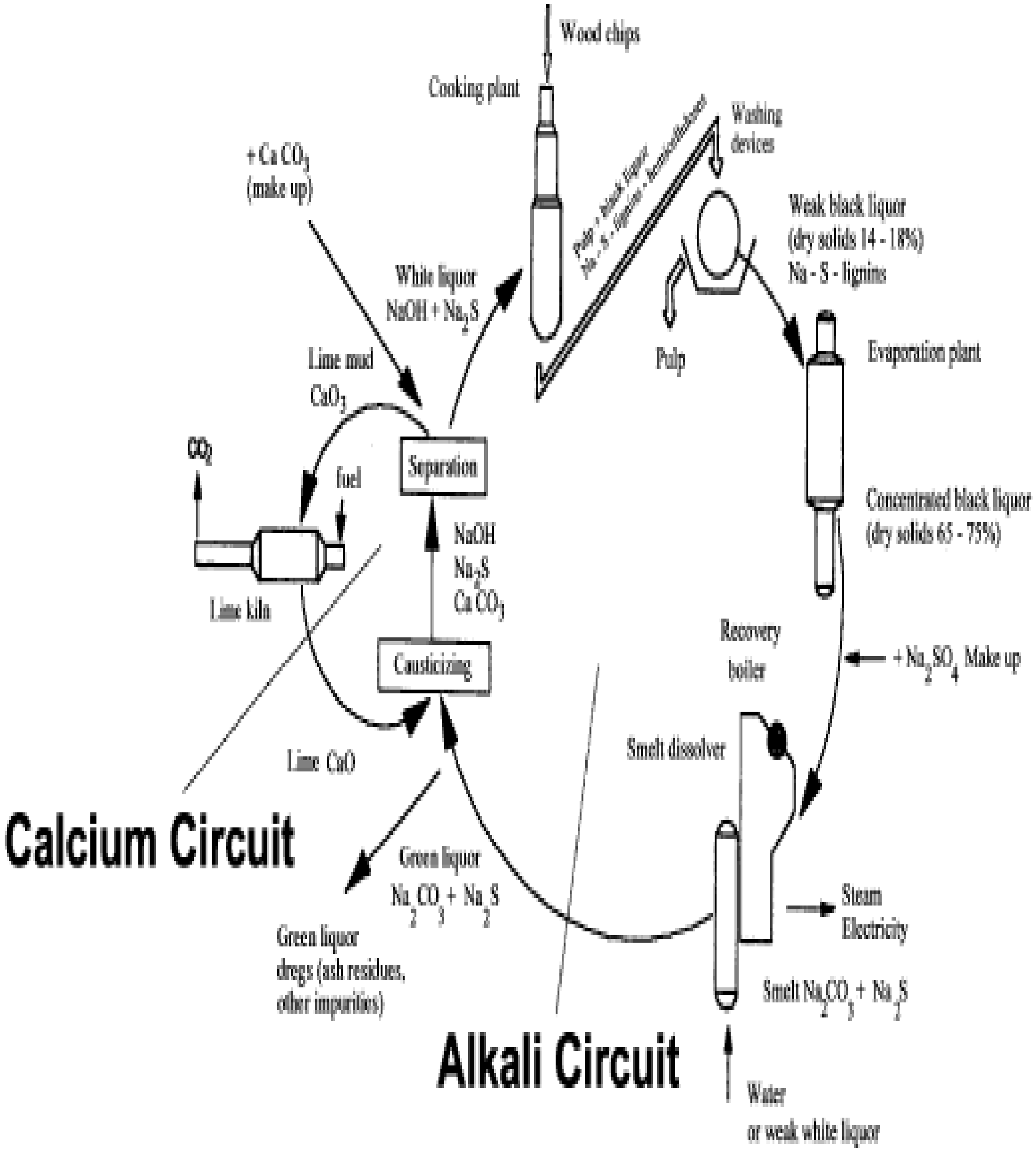


Figure 5: Recovery Cycles of Chemicals for a Kraft Mill

Black liquor from pulp washing normally has a dissolved solids content of 14 - 18% which has to be increased considerably before the liquor can be burnt. The liquor is concentrated in a multi-effect evaporation plant to a dry-solids content of 65 - 75% but as the dry-solids content increases, the viscosity of the black liquor increases and may become too high for pumping. At atmospheric pressure the upper limit is about 72 - 74% DS but two different principles are used to overcome the problem:

- pressurising the liquor, so that at a higher liquor temperature lowers the viscosity;
- changing the liquor rheology through a thermal depolymerization process.

The liquor can be concentrated to over 80% DS by using heat treatment on the strong black liquor and pressurised evaporation. In heat treatment some of the combustible material separates as non-condensable gases (NCG) which contain Total Reduced Sulphur (TRS). These gases are collected and burnt together with other malodorous gases.

Condensates from the black liquor evaporators and the cooking plant will vary in their degree of contamination according to origin but will typically contain TRS, methanol and some other volatile organic compounds. They are treated in a stripper column that is normally integrated with the black liquor evaporation by using secondary (or primary) steam. Stripping condensates makes it possible to reuse the condensate in washing unbleached pulp and in the causticizing plant.

The concentrated black liquor is burnt in the recovery boiler to recover the sodium and sulphur content in a suitable chemical form to regenerate the pulping chemicals and recover energy from the flue gases**.**

An increase in the dry-solids content of the black liquor from 65 - 70% to 80 - 85% changes the material and energy balances and the burning conditions in the recovery boiler. The flue gas flow decreases as less water enters the furnace. By increasing the dry-solids content to e.g. over 80% an increase in production or extended delignification with more efficient recovery of the black liquor can be possible in a mill where the recovery boiler is the production capacity bottleneck. The combustion temperature increases with higher DS feedstock and causes more sodium (Na) to be vaporised which then reacts with sulphur and reduces sulphur emissions from the recovery boiler.

The smelt from the recovery boiler is dissolved in water or weak white liquor to produce “green liquor” which consists mainly of sodium sulphide and sodium carbonate. The green liquor is clarified and causticized with lime where sodium carbonate is converted to sodium hydroxide to produce white liquor for pulping. Ash residues and other impurities are removed from the process as green liquor dregs. The calcium carbonate lime mud from causticizing is separated from the white liquor, washed and calcined in a lime kiln resembling somewhat a standard rotary cement kiln to regenerate the lime. This calcination is a high-temperature, endothermic reaction, requiring external fuel.

The handling and burning of black liquor with a high sulphur content releases sulphur into the air as sulphur dioxide and malodorous gases containing reduced sulphur compounds such as hydrogen sulphide (H_2S), methyl mercaptan (CH_3SH), dimethylsulphide (CH_3SCH_3) and dimethyldisulphide (CH_3SSCH_3).

Strong malodorous gases are collected and generally burnt in a separate burner or in the lime kiln. The latter is less favoured because it might upset the operation of the lime kiln. Flue gases are in most cases treated through a scrubber, and the scrubber water is led back to the chemical recovery system. Some Kraft pulp mills also collect weak malodorous gases to a varying extent. Weak gases are emitted from chip pre-steaming, screening, pulp washing, the smelt dissolver and tank ventilations etc.

4.3 Preparation of Bleaching Chemicals on Site

The most commonly used chemicals for bleaching of chemical pulps are chlorine dioxide, oxygen, ozone and peroxide. Chlorine dioxide and ozone have to be produced on site. Peroxide, oxygen and alkali can be delivered to the mills.

4.3.1 Chlorine Dioxide

Chlorine dioxide must be generated on site because it is unstable as a gas and can only be stored as a solution of approximately 1% in water. The gas stable at typical process temperatures of 40 to 70ºC and if the partial pressure of chlorine dioxide is kept below 100 mm Hg for at least five seconds. Once absorbed into solution chlorine dioxide can be stored for several months in the dark at -5ºC without any gas space. Gaseous chlorine dioxide decomposes to chlorine and oxygen and this decomposition is explosive at 300 mm Hg partial pressure.

There are a number of possible reactions to produce chlorine dioxide and some techniques can produce up to 0.7 tonnes of by-product chlorine per tonne of chlorine dioxide whilst others produce very small amounts. In pulp and paper industry chlorine dioxide is formed by acidic reduction of the chlorate ion ClO_3-.

Sodium chlorate is the common commercial source of the chlorate ion, but the choice of reducing agent has a great bearing on by-products and economics. Reducing agents, which have been used, include the chloride ion, hydrogen peroxide, sulphur dioxide and methanol.

Techniques have evolved over many years in order to maximise the yield of chlorine dioxide from the sodium chlorate, to minimise the formation of by-product chlorine and also to optimize the generation of waste acids. The two main techniques, which produce minimal by-product chlorine, are the Matheson process that uses sodium chlorate, sulphuric acid and sulphur dioxide; and the more recent SOLVAY derived R8 process, which principally uses sodium chlorate, sulphuric acid, and methanol. Additionally some chloride ion is essential for the generation of chlorine dioxide in all these processes. **Table 3** gives an overview about different chlorine dioxide generation methods.

Table 3: Chlorine Dioxide Generation Methods in Use in Finland

	MATHIESON	**R3**	**R3H**	**R5**	**R6**	**R7**	**R8**	**LURGI R6**
Input chemicals (t/t ClO_2)								
$NaClO_2$	1.75	1.6	1.68	1.75		1.68	1.65	
NaCl		8				0.35	0.03	1.08
H_2SO_4	1.30	1.1	0.80			0.40	1.10	
HCl		5	0.70	1.40				
SO_2	0.75	1.7				0.40		
CH_3OH		3					0.15	
Cl_2					1.80			
El power (MWh)					8.50			
By products (t/t ClO_2)								
$NaSO_4$	1.20	2.3	1.20			1.60		
H_2SO_4	1.60	0						
$Na_3H(SO_4)_2$							1.30	
Cl_2	0		0.70	0.80	0.30	1.20	0	0.10
H_2		0.7			0.05			
NaCl		0		0.95				
NaOH								0.70

Finnish BAT Report, 1997

It can be seen that only "Mathieson" and the so-called "R 8" technique does not produce chlorine as by-product.

Ideally any by-product sodium and sulphur from the generation of chlorine dioxide could be taken into the pulp mill as make-up chemicals and there would be very little or no effluent. However, if sodium or sulphur is produced in excess of the mill make-up requirements, they have to be removed from the process

A potential problem when ClO_2 is used is the formation of chlorate. About 10% of ClO_2 as active chlorine shows up a chlorate. This means that about 4-6 kg of chlorate is formed per t of pulp at ECF-bleaching at kappa 18. Chlorate is toxic to bacteria and plankton at levels of about 3-4 mg/l. In addition is inhibits growth of brown algae, e.g. bladder wrack, at concentrations from about 20 micrograms/l. The reason being that when N is the limiting factor for growth, algae take up chlorate, which is a known herbicide, instead of NO_3 -.

4.3.2 Ozone

Ozone is produced from dry air or oxygen by the application of high voltages (10 - 20 kV) across two electrodes separated by the reactant gas. Ozone is not very stable and the yield of ozone is fairly low with a high level of unreacted oxygen expected in the product gas. A modern ozone generator fed with oxygen uses about 10 - 15 kWh/kg O_3 generated.

4.3.3 Other Bleaching Chemicals

Other bleaching chemicals are bought in ready for use - Hydrogen Peroxide as 50% solution; Dithionite as a solid. Oxygen is mainly purchased but there are a few mills in Europe, which generate oxygen on site. In a few pulp mills in TCF-bleaching sequences peracetic acid is used as bleaching chemical. For the production of peracetic acid about 3 kWh electricity /kg of product is required.

5.0 SOURCES OF POLLUTION

The significant environmental impacts of the manufacture of pulp and paper result from the pulping and bleaching processes. In some processes, sulfur compounds and nitrogen oxides are emitted to the air, and chlorinated and organic compounds, nutrients, and metals are discharged to the wastewaters.

5.1 Air Emissions

In the kraft pulping process, highly malodorous emissions of reduced sulfur compounds, measured as total reduced sulfur (TRS) and including hydrogen sulfide, methyl mercaptan, dimethyl sulfide, are emitted, typically at a rate of

0.3-3 kilogram per metric ton (kg/t) of air-dried pulp (ADP) (air-dried pulp is defined as 90% bone-dry fiber and 10% water).
Other typical generation rates are: particulate matter, 75-150kg/t; sulfur oxides, 0.5-30 kg/t; nitrogen oxides, 1-3kg/t; and volatile organic compounds (VOCs), 15kg/t from black liquor oxidation.

Steam-and electricity-generating units using coal or fuel oil emit fly ash, sulfur oxides. Coal burning can emit fly ash at the rate of 100kg/t of ADP.

6.0 EMISSION CONTROL OPTIONS

The most significant environmental issues are the discharge of chlorine-based organic compounds (from bleaching) and of other toxic organics.The unchlorinated material is essentially black liquor that has escaped the mill recovery process. Some mills are approaching 100% recovery. Industry developments demonstrate that total chlorine-free bleaching is feasible for many pulp and paper products but cannot produce certain grades of paper. Wherever feasible, it is encouraged to adopt these modern process developments.

Pollution prevention programs should focus on minimizing air emissions. Process recommendations may include the following:-

i Use energy-efficient pulping processes wherever feasible. Acceptability of less bright products should be promoted. For less bright products such as newsprint, thermomechanical processes and recycled fiber may be considered.

ii Reduce bleaching requirements by process design and operation. Use the following measures to reduce emissions of chlorinated compounds to the environment: before bleaching, reduce the lignin content in the pulp (Kappa number of 10) for hardwood by extended cooking and by oxygen delignification under elevated pressure; optimize pulp washing prior to bleaching; use TCF or at a minimum, ECF bleaching systems; use of oxygen, ozone, peroxides (hydrogen peroxide), peracetic acid, or enzymes cellulose-free xylanase) as substitutes for chlorine-based bleaching chemicals; recover and incinerate maximum material removed from pulp bleaching; where chlorine bleaching is used, reduce the chlorine charge on the lignin by controlling pH and by splitting the addition of chlorine.

iii Minimize sulfur emissions to the atmosphere by using a low-odor design black liquor recovery furnace.

6.1 Examples of Measures for Reducing of Emissions to Air

1. Collection and incineration of concentrated malodorous gases from the fibre line, cooking plant, evaporation plant, condensate stripper, and control of the resulting SO_2. The strong gases can be burnt in the recovery boiler, the lime kiln or a separate, low NO_x fournace. The flue gases of the latter have a high concentration of SO_2 that is recovered in a scrubber.

2. Collection and incineration of diluted malodorous gases from e.g. the fibre line, various sources as tanks, chip bins, smelt dissolver etc. The weak malodorous gases can be burnt in e.g. the recovery boiler mixed with combustion air or in an auxiliary boiler depending on the volume.

3. Mitigation of the TRS emissions of the recovery boiler by computerised combustion control and CO measurement and in the case of the lime kiln by controlling the excess oxygen, by using low S-fuel, and by controlling the residual soluble sodium from the lime mud fed to the kiln.

4. Control of SO_2 emissions from the recovery boilers by firing high dry solids concentration black liquor in the recovery boiler to mitigate SO_2 formation and/or by using a flue gas scrubber.

5. Control of NO_x emissions from the recovery boilers and lime kiln by controlling the firing conditions and by ensuring proper mixing and division of air in the boiler, and for new or altered installations also by appropriate design;

6. Control of NO_x emissions from auxiliary boilers by controlling firing conditions and for new or altered installations also by appropriate design.

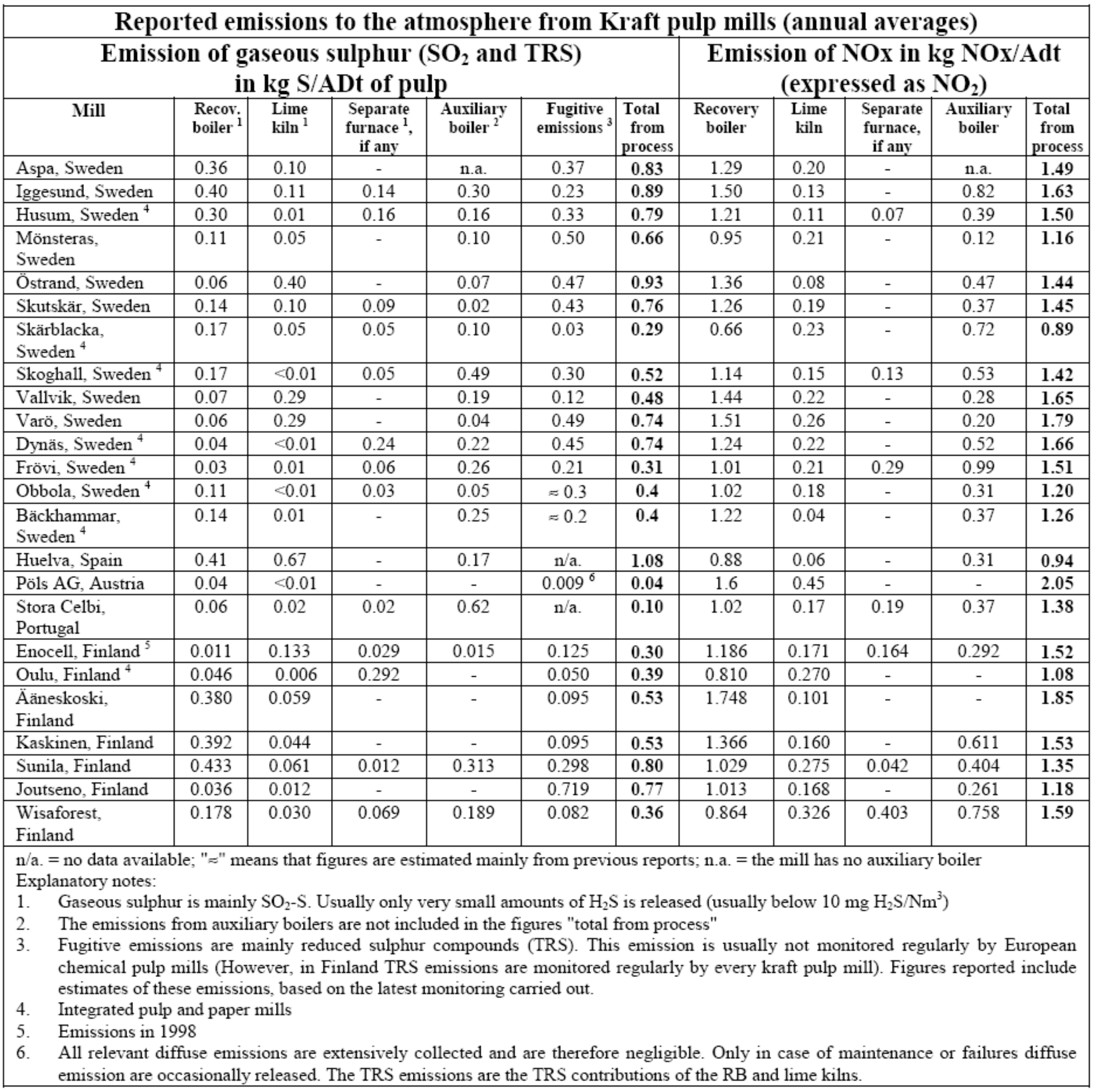
7. Reducing SO_2 emissions from auxiliary boilers by using bark, gas, low sulphur oil and coal or controlling S emissions with a scrubber.

8. Cleaning of the recovery boilers, auxiliary boilers (in which other biofuels and/or fossil fuels are incinerated) and lime kiln flue gases with efficient electrostatic precipitators to mitigate dust emissions.

A combination of these techniques result in a range of emissions for the major sources as shown in **Table 4**. The examples of mills stand for well performing mills in Europe that have implemented a reasonable set of these techniques. In all mill cases the gaseous emissions are cleaned with modern gas cleaning equipment as electrostatic precipitators and scrubbers according to practical application needs. Process related emissions cover recovery boiler (s), lime kiln (s), fugitive emissions and other furnaces (e.g. for TRS incineration) linked to the process, if any.

It should be noted that a direct comparison of the emission levels between countries is difficult due to uncertainties in the basis of data (lack of harmonisation in the methods of analysis and calculating emissions).

Table 4: Examples of Achieved Emission Levels to Air of Some Well Performing Existing Pulp Mills in Europe (Reference Year: 1997)



Reported emissions to the atmosphere from Kraft pulp mills (annual averages)

	Emission of gaseous sulphur (SO_2 and TRS) in kg S/ADt of pulp						**Emission of NOx in kg NOx/Adt (expressed as NO_2)**				
Mill	**Recov. boiler [1]**	**Lime kiln [1]**	**Separate furnace [1], if any**	**Auxiliary boiler [2]**	**Fugitive emissions [3]**	**Total from process**	**Recovery boiler**	**Lime kiln**	**Separate furnace, if any**	**Auxiliary boiler**	**Total from process**
Aspa, Sweden	0.36	0.10	-	n.a.	0.37	**0.83**	1.29	0.20	-	n.a.	**1.49**
Iggesund, Sweden	0.40	0.11	0.14	0.30	0.23	**0.89**	1.50	0.13	-	0.82	**1.63**
Husum, Sweden [4]	0.30	0.01	0.16	0.16	0.33	**0.79**	1.21	0.11	0.07	0.39	**1.50**
Mönsteras, Sweden	0.11	0.05	-	0.10	0.50	**0.66**	0.95	0.21	-	0.12	**1.16**
Östrand, Sweden	0.06	0.40	-	0.07	0.47	**0.93**	1.36	0.08	-	0.47	**1.44**
Skutskär, Sweden	0.14	0.10	0.09	0.02	0.43	**0.76**	1.26	0.19	-	0.37	**1.45**
Skärblacka, Sweden [4]	0.17	0.05	0.05	0.10	0.03	**0.29**	0.66	0.23	-	0.72	**0.89**
Skoghall, Sweden [4]	0.17	<0.01	0.05	0.49	0.30	**0.52**	1.14	0.15	0.13	0.53	**1.42**
Vallvik, Sweden	0.07	0.29	-	0.19	0.12	**0.48**	1.44	0.22	-	0.28	**1.65**
Varö, Sweden	0.06	0.29	-	0.04	0.49	**0.74**	1.51	0.26	-	0.20	**1.79**
Dynäs, Sweden [4]	0.04	<0.01	0.24	0.22	0.45	**0.74**	1.24	0.22	-	0.52	**1.66**
Frövi, Sweden [4]	0.03	0.01	0.06	0.26	0.21	**0.31**	1.01	0.21	0.29	0.99	**1.51**
Obbola, Sweden [4]	0.11	<0.01	0.03	0.05	≈ 0.3	**0.4**	1.02	0.18	-	0.31	**1.20**
Bäckhammar, Sweden [4]	0.14	0.01	-	0.25	≈ 0.2	**0.4**	1.22	0.04	-	0.37	**1.26**
Huelva, Spain	0.41	0.67	-	0.17	n/a.	**1.08**	0.88	0.06	-	0.31	**0.94**
Pöls AG, Austria	0.04	<0.01	-	-	0.009 [6]	**0.04**	1.6	0.45	-	-	**2.05**
Stora Celbi, Portugal	0.06	0.02	0.02	0.62	n/a.	**0.10**	1.02	0.17	0.19	0.37	**1.38**
Enocell, Finland [5]	0.011	0.133	0.029	0.015	0.125	**0.30**	1.186	0.171	0.164	0.292	**1.52**
Oulu, Finland [4]	0.046	0.006	0.292	-	0.050	**0.39**	0.810	0.270	-	-	**1.08**
Ääneskoski, Finland	0.380	0.059	-	-	0.095	**0.53**	1.748	0.101	-	-	**1.85**
Kaskinen, Finland	0.392	0.044	-	-	0.095	**0.53**	1.366	0.160	-	0.611	**1.53**
Sunila, Finland	0.433	0.061	0.012	0.313	0.298	**0.80**	1.029	0.275	0.042	0.404	**1.35**
Joutseno, Finland	0.036	0.012	-	-	0.719	**0.77**	1.013	0.168	-	0.261	**1.18**
Wisaforest, Finland	0.178	0.030	0.069	0.189	0.082	**0.36**	0.864	0.326	0.403	0.758	**1.59**

n/a. = no data available; "≈" means that figures are estimated mainly from previous reports; n.a. = the mill has no auxiliary boiler

Explanatory notes:

1. Gaseous sulphur is mainly SO_2-S. Usually only very small amounts of H_2S is released (usually below 10 mg H_2S/Nm^3)
2. The emissions from auxiliary boilers are not included in the figures "total from process"
3. Fugitive emissions are mainly reduced sulphur compounds (TRS). This emission is usually not monitored regularly by European chemical pulp mills (However, in Finland TRS emissions are monitored regularly by every kraft pulp mill). Figures reported include estimates of these emissions, based on the latest monitoring carried out.
4. Integrated pulp and paper mills
5. Emissions in 1998
6. All relevant diffuse emissions are extensively collected and are therefore negligible. Only in case of maintenance or failures diffuse emission are occasionally released. The TRS emissions are the TRS contributions of the RB and lime kilns.

NOTE:

The total process emissions do not include the auxiliary boilers. The list of mills is a selection of mills where data were available or provided and is therefore not intended to be complete. It contains rather mills from different pulping countries in Europe. The data are derived from environmental reports of the companies for 1997, personnel communication, SEPA report 4924 "The Forest Industry's emissions to water and air, amounts of waste and energy consumption, 1997"(in Swedish only) and from statistics of the Finnish Environment Institute. The method of analysing is the one used in the respective country

The balance between different gaseous emissions (SO_2, TRS, NO_x) and the recovery process itself should be kept in mind and carefully assessed when determining emission ranges. Depending on the type of the specific process-integrated measures implemented and the technical character of the mill the following atmospheric process emissions associated with the use of BAT can be generally achieved:

Table 5: Emission levels from the pulping process associated with the use of a suitable combination of best available techniques (emissions from any auxiliary boiler are not included).

Parameter	Units	Bleached and unbleached kraft pulp mills
TSP	kg/ADt	0.2 – 0.5
SO_2 as S	kgS/ADt	0.2 – 0.4
NO_x as NO2	kg/ADt	1.0 – 1.5
TRS as S	kgS/ADt	0.1 – 0.2

NOTE:

Process related emissions include recovery boiler(s), lime kiln(s), fugitive emissions and separate furnaces (e.g. for TRS incineration) linked to the process, if any. Values for bleached and unbleached Kraft pulp mills are not distinguished because there is no significant technical difference to consider

Table 5 should be read together with the following additional explanation. As far as concentrations of emissions are given they refer to daily averages and standard conditions of 273 K, 101.3 kPa and dry gas. The reference oxygen content is 5% for lime kilns and 5% for recovery boilers.

6.1.1 Dust Emissions

In kraft pulp mills, emission of particulates are controlled by electrostatic precipitators and sometimes also in SO_2 scrubbers. TSP emissions for recovery boilers between 30 - 50 mg/Nm^3 or 0.2 - 0.5 kg TSP/ADt (with a gas flow of 7000 - 9000 m^3/ADt) are considered as BAT. This level can generally be achieved by more modern recovery boilers by use of ESP only. Old recovery boilers achieve this level when they apply ESP and scrubbers.

However, scrubbers are mainly applied for removal of SO_2. 100-150 mg dust/m^3 is achievable at many existing mills which do not have a scrubber. With an SO_2-scrubber after the ESP, emissions at about 15 mg/Nm^3 are achievable.

For lime kilns 30 - 50 mg/Nm^3 or 0.03 - 0.05 kg/ADt (with a gas flow of 1000 m^3/ADt) can generally be achieved when using an ESP.

6.1.2 SO_2 Emissions

If changes in the fuel or the operation do not give enough reduction of SO_2 emission, removing sulphur oxides from flue gases by absorption in alkaline liquid is considered BAT. The removal efficiency for SO_2 is usually well above 90%.

- From recovery boilers equipped with a scrubber SO_2 emissions between 10 - 50 mg S/Nm3 or 0.1 - 0.4 kg S/ADt are achieved. Recovery boilers operating with high dry solid content of black liquor release very low SO_2 emissions normally below 0.1 kg S/ADt or down to 5 -10 mg S/Nm^3.

- The SO_2 emission levels of the lime kiln depend mainly on the fuel used, sulphur in the lime mud and whether NCG are also fed to the kiln. Oil fired kiln without NCG incineration achieves 5 - 30 mg SO_2/Nm^3 or 0.005 - 0.03 kg SO^2/ADt. Oil fired kiln with NCG incineration achieve 150 - 300 mg SO^2/Nm3 or 0.1 - 0.3 kg SO^2/ADt. Depending on the amount of sulphur (NCG) applied to the lime kiln a scrubber may be required. Another option for SO_2 reduction would be to choose another location for incineration of NCG than the lime kiln or use less sulphur containing oil burned as fuel.

6.1.3 NO_x Emissions

The emission of nitrogen oxides can be controlled by burner design (low NO_x burners) and modified combustion conditions (primary methods).

- The design of the recovery boiler (staged air feed systems) can result in relatively low NO_x concentrations. The recovery boiler is however responsible for the largest contribution to the total NO_x emission because of the large amount of liquors that are being burnt. Increased black liquor dry solids can lead to a slightly increase of NO_x emissions. Achievable emission levels are in the range of 80 - 120 mg NO_x/Nm^3 (40 - 60 mg NO_x/MJ) or 0.7 - 1.1 kg NO_x/ADt respectively. Process steam production is between about 13 and 18 GJ/ADt of pulp.

- The lime kiln is also a source of NO_x emission in kraft mills because of the high combustion temperature. In lime kilns the type of fuel also influences the NO_x formation. Higher NO_x levels are measured with gas firing than with oil firing. In oil firing the NO_x emission of the lime kiln is in the range of 100 - 200 mg/Nm^3 or 0.1 - 0.2 kg NO_x/ADt whereas gas fired kilns achieve 380 - 600 mg/Nm^3 or 0.4 - 0.6 kg NO_x/ADt. Combustion of malodorous gases in the lime kiln can also increase NO_x emissions. The possibilities to decrease the NO_x emissions by adjusting the kiln running parameters, the flame shape, the air distribution and the excess oxygen is limited but can lead to slight reduction of NO_x formation (about 10 - 20%).

- A separate furnace for TRS burning adds about 0.1 - 0.2 kg NO_x/ADt.

6.1.4. TRS Emissions (Malodorous Gases)

Pulp mill malodorous gases are collected and treated in different ways depending on the concentration and volume of the gases. The malodorous gas streams are divided into strong and weak gases. The systems for treatment of concentrated malodorous gases include a back-up system, which is activated when there are disturbances, maintenance or other downtimes of the normal system. Treatment methods for malodorous gases are incineration and alkaline scrubbing. There are different options for incineration of malodorous gases: lime kilns, dedicated incinerators or recovery boilers.

- When low volume concentrated malodorous gases are incinerated in the lime kiln, sulphur is partly absorbed. TRS emissions from the lime kiln are controlled by efficient lime mud washing and combustion condition control. A level of below 15 mg H_2S/Nm^3 (10% O2) can be achieved with a modern lime filter. If a further reduction of the TRS emissions is required an alkali scrubber must be installed after the ESP. This can bring the H_2S emissions down to about 1.5 mg/Nm^3 but is linked to a high consumption of alkali.

- Incineration of concentrated malodorous gases in a dedicated incinerator transforms TRS to SO_2 emissions. The incinerator therefore always has to be equipped with a scrubber.

- The incineration of concentrated gases in the recovery boiler operated with high solid content leads to very low sulphur emissions both SO_2 and TRS.

- High volume, diluted malodorous gases can be send to the recovery boiler where they are mixed into the secondary or tertiary combustion air or be burnt together with concentrated TRS in a separate dedicated burner. In lime kilns diluted malodorous gases can be mixed into the secondary air.

Besides the chosen gas treatment system the final TRS emissions are determined by the number of units that are connected to the gas collection system and the availability of the treatment system including back-up systems. Released fugitive TRS emissions consist mainly of noncollected diluted malodorous gases. The availability depends on the gas treatment system, the number and type of back-up systems and the monitoring and control of the system. High availability of the gas treatment system can be achieved for instance by:

- use of a dedicated incinerator with SO_2 scrubber as the major unit and by use of the lime kiln or an alkaline scrubber as one back-up and a flare as a second back-up.

- incineration of the strong and weak gases in the recovery boiler and use of the lime kiln as one back-up and a flare as a second back-up.

6.1.5 Auxiliary Boilers

Emission levels associated with BAT from auxiliary boilers are given in **Table 6**. The total releases to air are very site specific (e.g. type of fuel, integrated or market pulp mill, production of electricity). It should be noted that many mills use fuel mixes.

Table 6: Emission Levels Associated with the Use of BAT for Different Fuels

Released substances	Coal	Heavy fuel oil	Gas oil	Gas	Biofuel (e.g. bark)
Mg S/MJ fuel input	100 – 200 [1] (50 – 100) [5]	100 – 200 [1] (50 – 100) [5]	25 - 50	<5	<15
Mg NO_x/MJ fuel input	80 – 110 [2] (50–80 SNCR)[3]	80 – 110 [2] (50–80 SNCR)[3]	45–60 [2]	30–60 [2]	60 – 100 [2] (40–70 SNCR)[3]
Mg dust/Nm^3	10 – 30 [4] at 6% O_2	10 – 40 [4] at 3% O_2	10 – 30 3% O_2	<5 3% O_2	10 – 30 [4] at 6% O_2

Notes:
1. Sulphur emissions of oil coal fired boilers depend on the availability of low-S oil and coal. Certain reduction of sulphur could be achieved with injection of calcium carbonate.
2. Only combustion technology is applied
3. Secondary measures as SNCR are also applied; only larger installations
4. Achieved values when electrostatic precipitators are used
5. When a scrubber is used; only applied to larger installations

It is noted that auxiliary boilers within the pulp and paper industry are in various sizes (from 10 to above 200 MW).

In a modern non-integrated mill the heat generated from black liquor and incineration of bark exceeds the energy required for the entire production process. However, fuel oil will be needed at certain occasions like start-up and also at many mills in the lime kiln.

7.0 RECOMMENDED PRACTICES AND EMISSION VALUES

The key production and control practices that will lead to compliance with emissions guidelines can be summarized as follows:-

i Prefer dry debarking processes.
ii Prevent and control spills of black liquor.
iii Prefer total chlorine-free processes, but at a minimum, use elemental chlorine-free bleaching systems.
iv Reduce the use of hazardous bleaching chemicals by extended cooking and oxygen delignification.
v Aim for zero-effluent discharge where feasible. Reduce wastewater discharges to the extent feasible. Incinerate liquid effluents from the pulping and bleaching processes.
vi Reduce the odor from reduced sulfur emissions by collection and incineration and by using modern, low-odor recover boilers fired at over 75% concentration of black liquor.
vii Dewater and properly manage sludges.
viii Where wood is used as raw material to the process, encourage plantation of trees to ensure sustainability of forests.

Emissions levels for the design and operation of each project must be established through the environmental assessment (EA) process on the basis of country legislation. The emissions levels given here can be consistently achieved by well-designed, well operated, and well maintained pollution control systems.

The guidelines are expressed as concentrations to facilitate monitoring. Dilution of air emissions or effluents to achieve these guidelines is unacceptable.

All of the maximum levels should be achieved for at least 95% of the time that the plant or unit is operating, to be calculated as a proportion of annual operating hours.

7.1 Air Emissions

Air emissions from pulp and paper manufacturing should achieve the levels presented in **Table 7.**

Table 7: Air Emissions from Pulp and Paper Manufacturing

Parameter	Maximum value (milligrams per normal cubic meter)
PM[a]	100 for recovery furnace
Hydrogen sulfide	15 (for lime kilns)
Total sulfur emitted a. Sulfite mills b. Kraft and other	 1.5 kg/t ADP 1.0 kg/t ADP
Nitrogen oxides	2 kg/t ADP

[a]. Where achieving 100 mg/Nm^{3}is not cost-effective, an emissions level up to 150 mg/Nm^3 is acceptable. Air emissions requirements are for dry gas, at 0°C and 1 atmosphere.

8.0 EMISSION MONITORING AND REPORTING

Frequent sampling may be required during start-up and upset conditions. Once a record of consistent performance has been established, sampling for parameters listed in this document should be as described below:-

i Monitoring of air emissions for opacity (maximum level of 10%) should be continuous; daily monitoring should be conducted for hydrogen sulfide and annual monitoring for other pollutants. Liquid effluents should be monitored for the listed parameters at least daily, or more often when there are significant process changes.

ii Monitoring data should be analyzed and reviewed at regular intervals and compared with the operating standards so that any necessary corrective actions can be taken. Records of monitoring results should be kept in an acceptable format. The results should be reported to the responsible authorities and relevant parties, as required.

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