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EXPERT GROUP ON BEST AVAILABLE
TECHNIQUES AND BEST ENVIRONMENTAL
PRACTICES

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Item 3 of the provisional agenda¹

Development of guidelines on best available techniques and provisional guidance on best environmental practices relevant to the provisions of Article 5 and Annex C of the Stockholm Convention on Persistent Organic Pollutants

DRAFT GUIDELINES ON BEST AVAILABLE TECHNIQUES
FOR PULPING PROCESSES

Note by the Secretariat

The attached was submitted by Ms. Hille Hyytiä (Finland) who coordinated its development. This note and the attached have not been formally edited.

¹ UNEP/POPS/EGB.2/1.

Draft Guidelines on Best Available Techniques (BAT) for Pulping Processes

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Pulping Processes – Look Up Table

The following table is a summary of the draft guidance:

BAT only applies to new plant and plant undergoing a significant change. The emission limits are invoked for existing plant when significant changes take place.

See Appendix 1 for further details of each technique.



Future options, investment or process status dependent improvements.

Measure	Technique	New Source BAT	Existing Source BEP
Emission Limits AOX to water.	AOX after biological treatment BAT - 0.25 kg/Adt.	✓	BEP achieves significant reductions. Significant change invokes BAT.
Emission Limits PCDD / PCDF to water.	PCDD - Less than measurable limit. PCDF – 31.9 ng/m ³ Max.	✓	BEP achieves significant reductions. Significant change invokes BAT.
Emission Limits PCDD / PCDF to air.	PCDD/F – 0.1 ng/m ³ .	✓	BEP achieves significant reductions. Significant change invokes BAT.
Chemical Pulping Process selection. Process amenable to low environmental impact acceptable bleaching regimes.	1. Fibre type pulping process selection to achieve a lower environmental impact in bleaching.	✓	
Chemical Pulping Reduce effluent load of bleachery. Reduce kappa via efficient cooking.	2. Optimum raw fibre materials handling and preparation.	✓	✓
Chemical Pulping Reduce effluent load of bleachery. Reduce kappa via efficient cooking.	3. Use of cooking catalysts.		
Chemical Pulping Reduce effluent load of bleachery. Reduce kappa number via extended delignification.	4. Extended (modified) cooking - Batch digestion.	✓	
Chemical Pulping Reduce effluent load of bleachery. Reduce kappa number via extended delignification.	5. Extended (modified) cooking - Continuous digestion.	✓	
Chemical Pulping Reduce effluent load of bleachery. Reduce kappa number via extended delignification.	6. Sulphite pulping options.	✓	
Chemical Pulping Reduce effluent load of bleachery. Reduce kappa number via extended delignification.	7. Hot alkali extraction.		
Chemical Pulping Reduce effluent load of bleachery. Reduce carry over to bleaching via efficient washing.	8. Efficient brown stock washing and closed screening.	✓	✓
Chemical Pulping Reduce effluent load of bleachery. Reduce carry over to bleaching via efficient washing.	9. Eliminate synthetic dioxin precursors.	✓	✓
Chemical Pulping Reduce effluent load of bleachery. Reduce kappa number via oxygen delignification.	10. Oxygen delignification.- non wood fibres.	✓	
Chemical Pulping Reduce effluent load of bleachery. Reduce kappa number via oxygen delignification.	11. Oxygen delignification – wood fibres.	✓	
Chemical Pulping Reduce effluent load of bleachery. Reduce kappa number via other pre bleaching	12. Pre bleach - Enzyme pre treatment.		

treatments.			
Chemical Pulping Reduce effluent load of bleachery. Reduce kappa number via other pre bleaching treatments.	13. Pre bleach treatments - Acid hydrolysis.		
Bleaching Reduce effluent load of bleachery. Increase substitution and replace chlorine and hypochlorite with chlorine dioxide.	14. Chlorine optimisation and chlorine dioxide substitution.		
Bleaching Reduce effluent load of bleachery. Increase substitution and replace chlorine and hypochlorite with chlorine dioxide.	15. Chlorine manufacture and handling.		
Bleaching Reduce effluent load of bleachery. Increase substitution and replace chlorine and hypochlorite with chlorine dioxide.	16 + 17. ECF Bleaching.		
Bleaching Reduce effluent load of bleachery. Increase substitution and replace chlorine and hypochlorite with chlorine dioxide.	18. Chlorine dioxide manufacture.		
Bleaching Reduce effluent load of bleachery. Enhance lignin removal before chlorine dioxide stage.	19. Reinforced alkaline extraction.		
Bleaching Reduce effluent load of bleachery. Use of ECF and TCF bleaching.	20. Acid chelation.		
Bleaching Reduce effluent load of bleachery. Use of ECF and TCF bleaching.	21. Increase bleach plant closure.		
Bleaching Reduce effluent load of bleachery. Use of ECF and TCF bleaching.	22. De-bottlenecking recovery boiler.		
Bleaching Reduce effluent load of bleachery. Use of ECF and TCF bleaching.	23. De-bottlenecking chlorine dioxide manufacture.		
Bleaching Reduce effluent load of bleachery. Use of ECF and TCF bleaching.	24. TCF bleaching.		
Bleaching Reduce effluent load of bleachery. Use of ECF and TCF bleaching.	25. Hydrogen Peroxide.		
Bleaching Reduce effluent load of bleachery. Use of ECF and TCF bleaching.	26. Ozone.		
Bleaching Reduce effluent load of bleachery. Use of ECF and TCF bleaching.	27. TCF Sequences (Existing plant).		
Bleaching Reduce effluent load of bleachery. Use of ECF and TCF bleaching.	28. TCF Sequences (Using Peroxide).		
Bleaching Reduce effluent load of bleachery. Use of ECF and TCF bleaching.	29. TCF Sequence (Peroxide and Ozone).		
Bleaching Reduce effluent load of bleachery. Use of ECF and TCF bleaching.	30. TCF Sequences (Ozone and Reinforced Peroxide).		
Effluent treatment Reduce effluent emissions to water. Treat effluents to degrade organics; adsorb persistent organics onto sludge.	31. Primary and biological treatments.		
Effluent treatment Reduce effluent emissions to water. Treat effluents to degrade organics; adsorb persistent organics onto sludge.	32. Spill Control.		

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Recovery Combustion processes. Combustion control.	33. De inking sludge management.	✓	✓
Recovery Combustion processes. Combustion control.	34. Recovery boiler.	✓	✓
Recovery Combustion processes. Combustion control.	35. Sludge combustion.	✓	✓
Recovery Combustion processes. Combustion control.	36. Auxiliary boilers / bark boilers.	✓	✓
Others	37. Transport.	-	✓
Others	38. Fibre selection and storage.	✓	✓
Others	39. Effluent treatment sludge management.	✓	✓
Others	40. Combustion flue dust management.	✓	✓

Pulping Processes

1 Process Description

In general terms, pulp and paper are manufactured from raw materials containing cellulose fibres, generally wood, recycled paper and many types of agricultural residue. Wood and the main nonwood fibres used in papermaking are a complex mixture of the same substances – cellulose (40-45%), hemicelluloses (25-35%), lignin (20-30%) and extractives (2-15%). Generally speaking, most ligno-cellulosic and cellulosic materials of fibrous structure may be processed into various grades of papers and paperboard. Fibres from different raw materials are, however, not alike. They differ considerably in their morphological and chemical characteristics, which make them more or less suitable for papermaking.

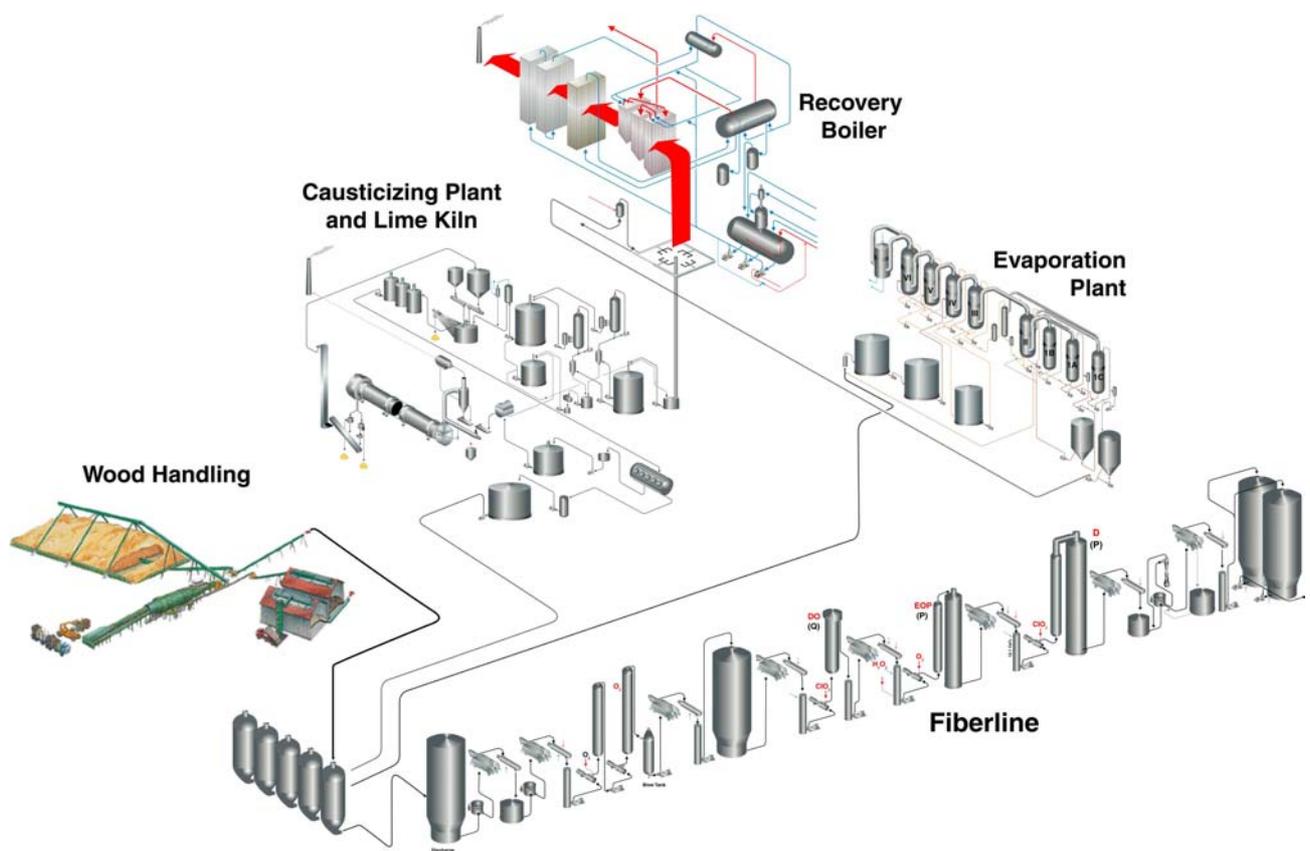


Figure 1. Example of a modern ECF kraft wood pulping mill - Courtesy of Metso Automation Inc. 2003

1.1 From fibres, to Pulp, to Paper

Different paper and paperboard product categories need specific pulp properties and the most appropriate manufacturing route to produce these products differs substantially. For instance, newsprint is a high volume product of moderate strength, opacity and printability and a relatively short life. Therefore, a high yield of pulp at the expense of maximum achievable strength and brightness can be manufactured from the raw materials and there is a lower bleaching requirement due to natural brightness of the pulps. On the other hand packaging papers need strength if they are to be fit for use and here it is necessary to accept a lower yield via a different manufacturing route in order to obtain this strength but again the bleaching requirement may be low if this is a middle layer board. Further characteristics such as the brightness and its durability as required by outer packaging layers and printing and writing papers that may need to last for many years

without yellowing, mean that and here the level of delignification and bleaching applied may need to be high. The amount of effort needed in bleaching can therefore vary widely.

Pulping and bleaching technology must be matched to the quality and characteristics of the pulp and paper to be produced. No single pulping or bleaching process can produce pulp suitable for all uses.

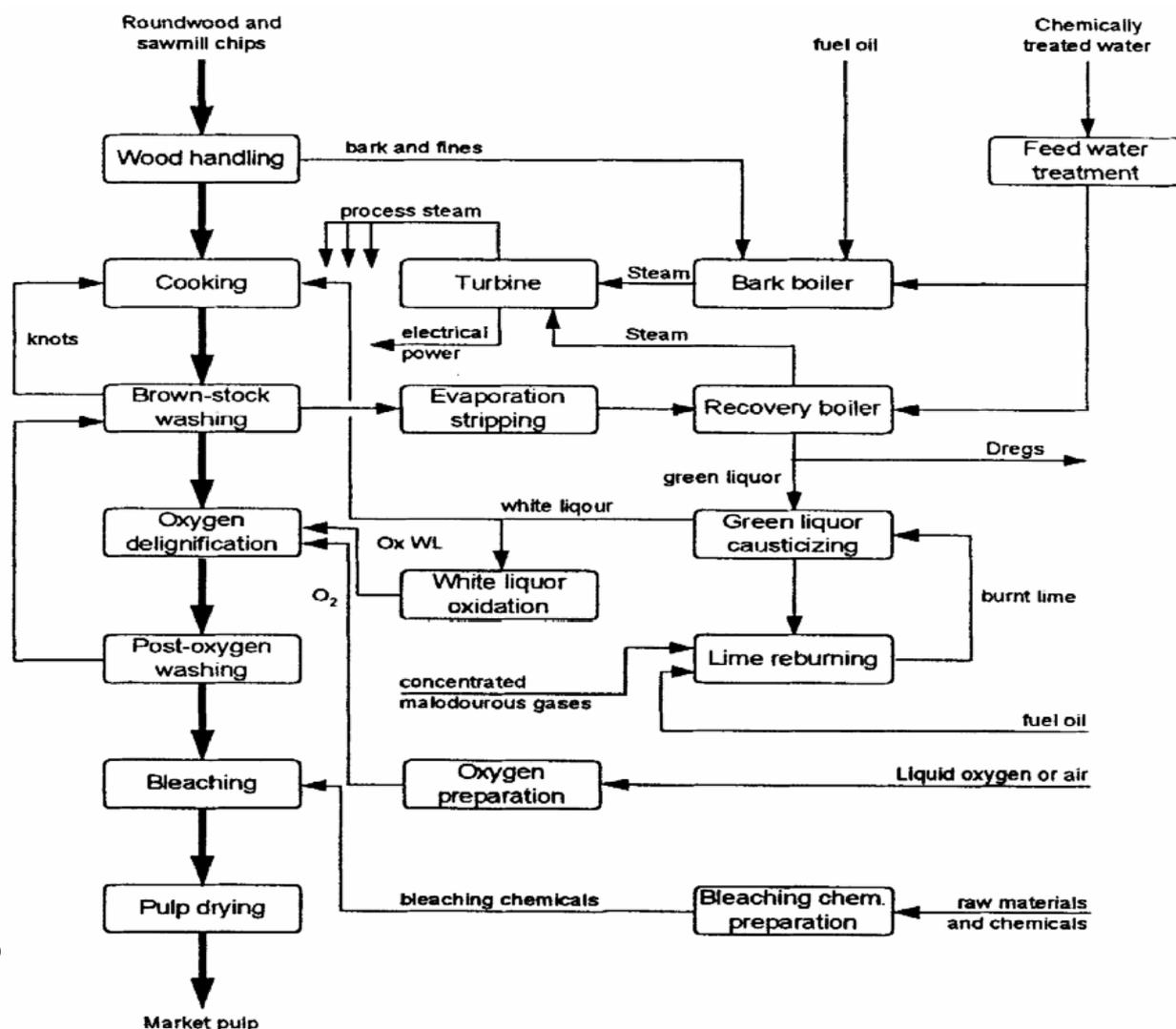
The question of what kind of pulping process to apply and how to bleach the resulting pulps needs therefore to be prefaced with the question: "What fibre raw materials are we starting with and what are the required end product (paper) characteristics?"

1.2 Fibre Types

Apart from hardwood and softwood species normally used in pulping, in some parts of the world a very high proportion of primary cellulose fibres originate from nonwood raw materials such as bagasse, cereal straw, bamboo, reeds, grasses, jute, kenaf, flax and sisal [TAPPI, 1987]. Over 10% of world pulp production is made from these non wood fibres and in some countries it is the dominant fibre source, for instance in China and India.

The technical-economic relationships which have led to the predominance of wood fibres in many countries do not apply everywhere. Indeed, non wood pulping capacity is increasing faster than wood pulping capacity. In this respect Southeast Asian markets are likely to grow and lead the world's paper consumption in the future. Non wood plant fibres will therefore play an increasing role in the world's pulp and paper industry and so an attempt has been made to include non wood issues here, as much as possible. The proportion of recycled fibres being re introduced into the paper manufacturing cycle is also increasing rapidly with major trade links for recovered fibre between countries.

Figure 2. Pulping Process Flows – Kraft Pulping Example [EIPPCB BREF, 2001]



1.3 Process Steps

The main processes involved in making pulp, cellulose and paper products are: raw material handling and preparation, such as transport, storage, wood debarking, chipping and agricultural residue cleaning and de-noding; then pulping; pulp processing and bleaching and then paper or paperboard making. Cellulose rich pulp products are also manufactured as raw material for other industrial processes, the manufacture of rayon, cellophane and some products in the chemical industry for example.

The industry is a divergent production process (unlike classical component assembly industries) and so there is a wide range of techniques, using different pulping chemicals and process conditions as well as different bleaching sequences, that deliver the desired fibre product characteristics from a range of available raw fibre types and mixtures. The methods employed vary across the world both in relation to the characteristics of the fibre types available, the products to be made from them and the local pollution control restrictions that apply.

1.4 Scale of Production

A further difference in relation to the scale of production is seen in different parts of the world with the capacities ranging from small mills of a few tens of tonnes per day through to major industrial complexes processing 1,000 to 1,500 tonnes per day. For example, in China the average mill size is 6,000 tonnes per year compared to over 40,000 tonnes per year as a world average.

1.5 Mill Types

Pulp and paper mills may be integrated or non-integrated. Non-integrated pulp mills (market pulp) are only manufacturing pulp that is then sold on the open market. Non-integrated paper mills use purchased pulp for their paper production. In integrated pulp and paper mills, the activities of pulp and paper making are undertaken on the same site. Compared to pulp production a relatively high number of small and medium-sized paper manufacturing facilities are in operation in many countries. With recovered paper manufacturing the level of integration is high; nearly all recovered paper mills include recovered paper processing, some of them adding purchased pulp.

1.6 Pulping Methods Applied

The manufacture of pulp uses mechanical, thermomechanical, chemimechanical and chemical methods. Mechanical and thermomechanical methods are used in integrated mills to make naturally bright, high yield pulps mainly used for newsprint manufacture. Chemical methods are used in integrated and non integrated pulping mills. The main chemical semi-chemical and chemimechanical pulping techniques are:

- **Lime, lime-soda** especially non wood fibres;
- **Cold soda** uses sodium hydroxide pre treatment at ambient temperatures, alone or with sodium carbonate; especially hardwood and nonwood fibres; (semi chemical).
- **Soda AQ** sodium hydroxide alone or with sodium carbonate and a catalyst anthraquinone, hardwood and nonwood fibres; (chemical, similar to kraft but without sulphur), reduced odour.
- **Sulphate (kraft)** uses a mixture of sodium hydroxide and sodium sulphide under alkaline conditions to dissolve the lignin, wood and most non wood fibres; (chemical method).
- **Sulphite - acid bisulphite, bisulphite, alkaline and neutral sulphite methods**, (Ca, Mg, NH₄, Na) different bases, including anthraquinone, under a range of pH, to dissolve the lignins, most wood fibres; (chemical and semi-chemical methods).
- **Organosolv** methods, wood and nonwood applications, some proven on mill scale:
 - **Alcohol** as a solvent,;

- **Organic acids** as solvent;
- **Hybrid processes.**

In chemical pulping, chemicals are used in a cooking process to dissolve the lignin which surrounds the fibres. The lignin and many other organic substances are thus put into solution. In mechanical pulping processes, mechanical shear forces are used to pull the fibres apart and the majority of the lignin remains with the fibres, although there is still some significant dissolution of organics. Pulps produced in different ways have different properties that make them suited to particular products.

Pulping is the process of converting the virgin fibre into a form suitable for making paper and paper board grades. In chemical pulping the fibres are broken down chemically in pressure vessels, called digesters, which in the case of batch processes are heated, pressure vessels, usually arranged to rotate to unload the contents or in the case of are continuous processes are vertical tower type constant flow digesters. Mechanical pulping processes use grinding or chipping followed by disc refining and direct supply to a paper machine.

During processing, more of the wood (mainly lignin) is removed in chemical pulping, therefore yields (kg pulp/kg timber) are less than with mechanical pulping. Some mechanical properties are better compared to mechanical pulps however, as the fibres are not mechanically damaged and the lack of lignin produces a whiter, more stable paper. Most large chemical pulp mills using the kraft process recover the pulping chemicals and the wood organics from the liquor where the process chemistry allows this. The lost yield forms the high organics load in the cooking liquors which are used for a variety of products or, more normally, as process fuel for steam and power generation by burning the concentrated cooking liquors in a recovery furnace. The inorganic process chemicals are also recovered at the same time as an inorganic melt from which and fresh cooking chemicals can be regenerated. Many small mills do not recover the liquor. The recovery of non wood fibre liquors is problematic due to high silica content of fibre materials. However, this area of recovery technology is currently receiving much attention with some claims for viable processes.

1.6.1 Lime and Soda processes

These are processes using simple alkaline cooking liquors in a similar process to kraft pulping but without the use of sulphur compounds. At mills with no chemical recovery, all the dissolved wood substances and pulping/bleaching chemicals remain in the wastewater apart from the volatiles incidentally released to atmosphere. The de-lignification ability is inadequate for low yield, high white, wood pulping. Its application to non-wood pulps is widespread and it is also used with oxygen for straw pulping. In the soda process, the chemistry is simplified as there is no added sulphur to form undesirable by-products and the hydroxide can be recovered by lime causticisation of the sodium carbonate smelt. After cooking, pulps that are not to be bleached are refined to separate the fibres.

1.6.2 The Kraft (Sulphate) Pulping Process

The kraft or sulphate process is an alkaline cooking liquor process and it is the dominating pulping process world wide (84 % of the world chemical pulp production and 63% of total chemical and mechanical pulp production). The kraft process uses a sodium based alkaline pulping solution consisting of sodium sulphide (Na_2S) and sodium hydroxide (NaOH). Used cooking liquor (black liquor) is recovered to generate white liquor for the first pulping step. At mills with chemical recovery, most of the dissolved wood substances are combusted and the wastewater mainly contains the organics in condensates plus, at bleached mills, the substances dissolved during bleaching and the residues of the bleaching chemicals.

1.6.3 Sulphite Pulping Processes

The sulphite pulping process is based on aqueous sulphur dioxide (SO₂) and a base, calcium, sodium, magnesium or ammonium. This method is losing its importance and only 10% of the world pulp is produced by this method. Alkaline sulphite mills for non wood fibres are often operated as a batch process and chemical recovery is generally not practised at such mills due to their small size and the complexity of chemical recovery from what is normally a sodium based process. Relatively bright and easily bleached pulps. Easy to bleach without chlorine chemicals.

1.6.4 Other Pulping Processes

The development of pulping with ethanol or methanol mostly sulphur-free processes has been an area of novel pulping research as in the **Alcell**, **Organocell** and **ASAM** (some sulphite used) processes, but none have yet proceeded to a viable full-scale installation. Another similar process is **Milox** using formic acid and hydrogen peroxide. Some of these processes are looking to areas of application in the pulping of non wood fibres where they may offer solutions to overcome some of the recovery cycle technical difficulties.

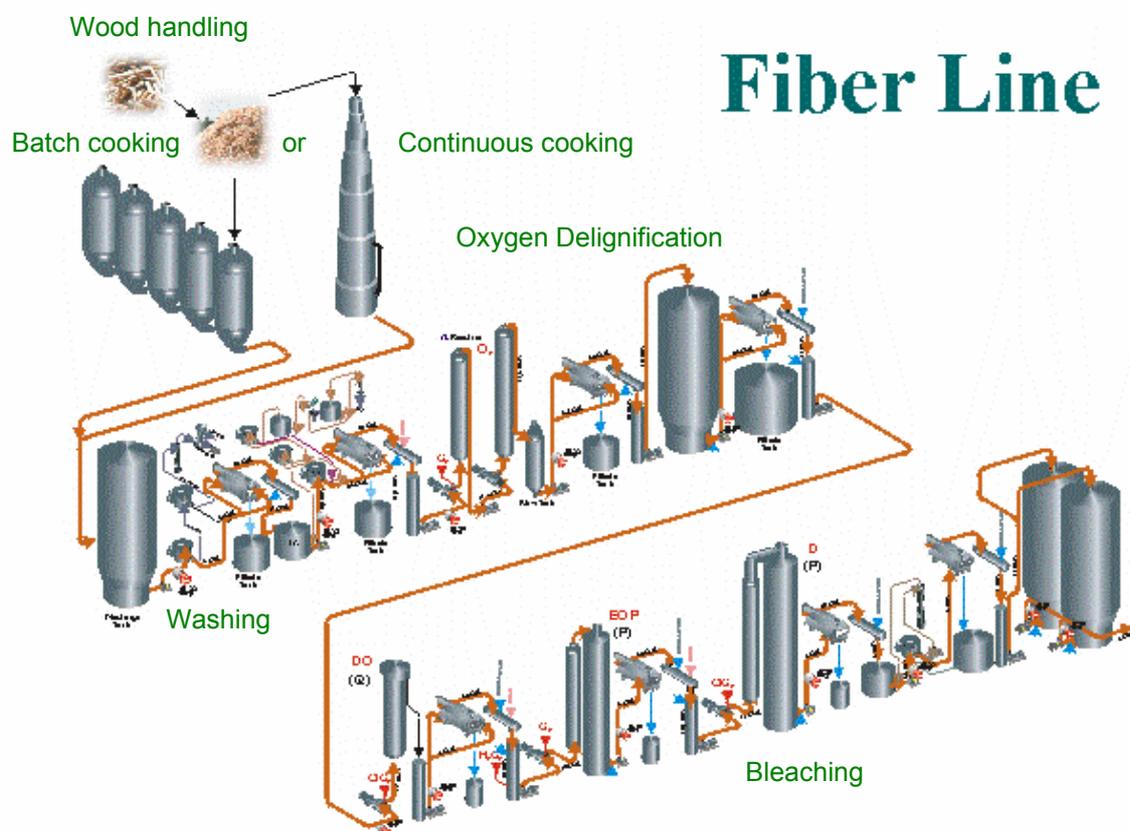


Figure 3. Example of a modern ECF fibre line - Courtesy of Metso Automation Inc. 2003

1.7 Bleaching

Bleaching (optional depending on intended paper grade), then whitens the pulp either by removing more lignin (for chemical pulps) or by changing the chemical structure of lignin (mechanical pulps). Mechanical pulps can often be used without bleaching, but where brightening is done it is achieved using non chlorinated compounds such as dithionite or peroxides. However, with chemical pulps the objective of bleaching is to further remove the small quantity of residual lignin left after cooking. Hardwood and straw pulps are easier to bleach by non chlorine methods due to their lower lignin content to begin with. Residual lignin is converted into soluble forms by the application of further

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delignification and bleaching stages using combinations of oxygen, hydrogen peroxide, ozone, peracetic acid, Caro's acid, sodium hypochlorite, chlorine dioxide, chlorine and other chemicals or treatments. Sodium hydroxide is used to perform the extractions of the soluble lignin compounds from the pulp. Water is used to perform intermediate washes to remove extracted wastes from the pulp.

To remove the colour associated with remaining residual lignin, the pulp is bleached in three to five stages, the first two stages primarily releasing and extracting lignin and the subsequent stages for removing the lignin residues and finishing the product. The bleaching effort required for sulphite pulps is less due to higher pre bleach brightness. A bleach plant consists of a sequence of separate bleaching stages with different chemicals or combination of chemicals added. All lignin cannot be removed selectively enough in a single bleaching stage, but several subsequent stages with intermediate washing have to be used. These bleaching sequences are applied to maximise the bleaching effect of each component. Bleaching sequences where chlorine based chemicals are used are called Chlorine Chemical Bleaching (CCB). If molecular chlorine and hypochlorite are excluded, the abbreviation is Chlorine Dioxide Bleaching (CDB), or Elemental Chlorine Free (ECF). If the sequence uses only oxygen based chemicals like oxygen, alkaline or acidic peroxide the term Oxygen Chemical Bleaching (OCB), or Totally Chlorine Free (TCF) can be used.

The notations ECF and TCF therefore only indicate what is not principally used in the sequence. The ECF bleaching term is troublesome as there still may be some elemental chlorine generated in bleaching reactions or present in the chlorine dioxide used.

ECF pulp bleached with chlorine dioxide accounts for the predominant share of roughly two-thirds of the bleached pulp produced world-wide. TCF pulp only accounts for about 6% and is primarily produced in mills in Northern and Central Europe. Roughly 25% of the pulp produced world-wide is still bleached with elemental chlorine

1.8 Recycled Fibre Pulping.

Mechanical cleaning with or without de-inking is the analogous process for cleaning up recovered papers (most recovered paper is recycled without de-inking). These fibres may be dirty / contaminated but have less of a bleaching requirement. However, there is a trend for increasing concentrations of mechanical fibres in recycled paper feedstock.

1.9 Other Activities.

Papermaking then converts the pulped cellulose fibres into paper or paperboard on a paper machine. Coating (optional) uses water-based or solvent-based coatings to impart special optical or structural properties to papers as required.

1.10 Emissions

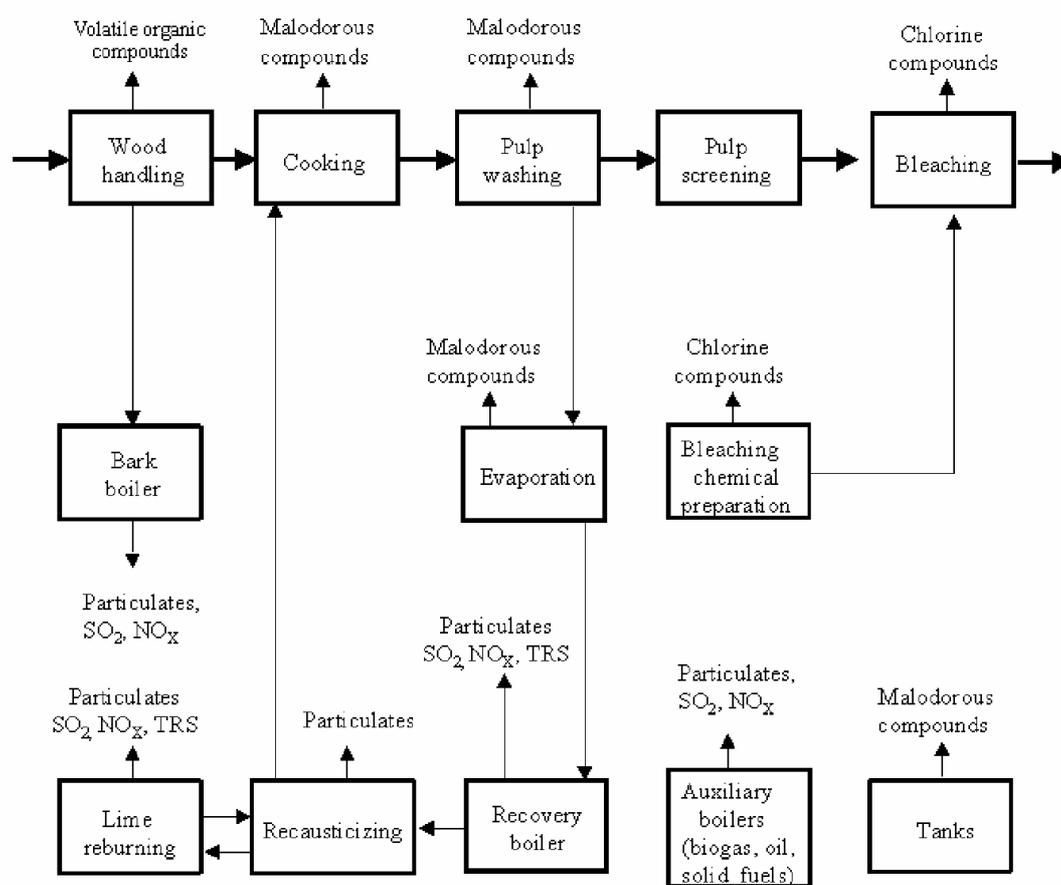


Figure 4 Emissions to water, kraft pulp mill example - [IIPPCB BREF, 2001]

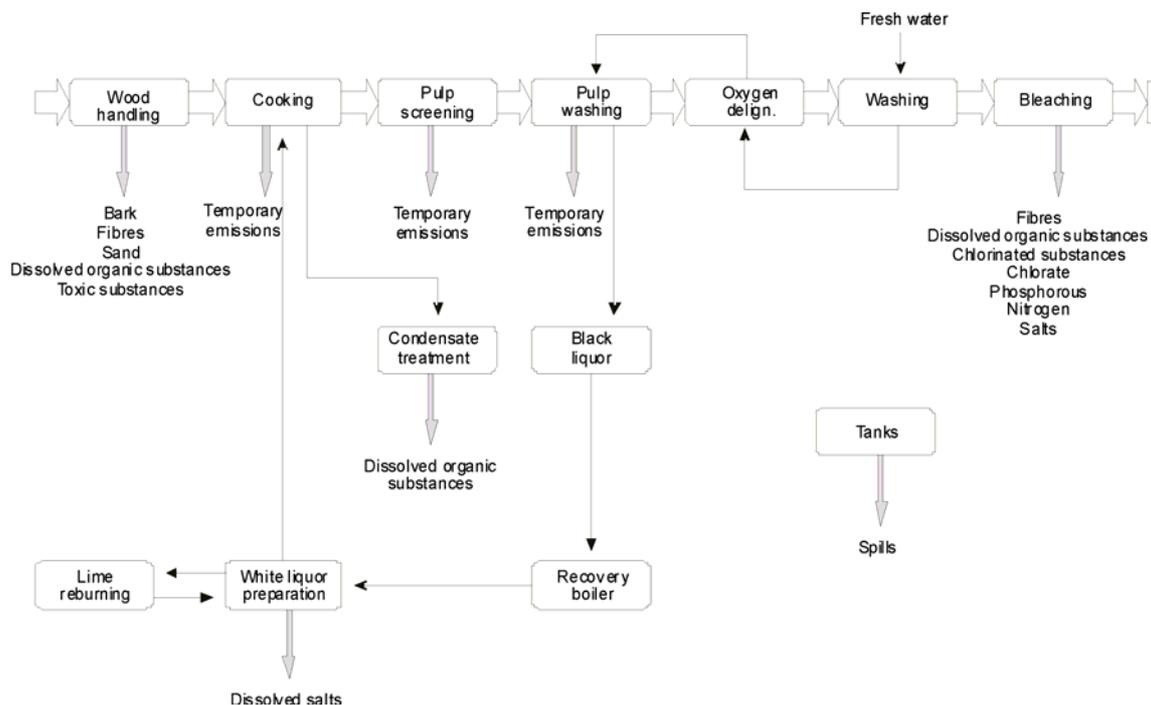


Figure 5 Emissions to air, kraft pulp mill example - [IIPPCB BREF, 2001]

2 Sources of Unintentionally Produced POPs (UPOPs)

2.1 Background

Over the last 20 years one of the main issues in pollution control within the pulp and paper sector has been on the role of chlorinated substances formed in the bleach plant. The detection of dioxins and furans in effluents from pulp mills and the harmful effects of chlorine bleaching have acted as drivers to encourage decreases in the use of molecular chlorine as a bleaching chemical.

The use of AOX loading in the following guidance is not meant to imply that AOX is an appropriate measure of the performance of any in-process and end-of-pipe technology in reducing the level of specific chlorinated organic pollutants such as dioxin and furan found in wastewaters, but it is used instead, to illustrate which process changes and treatment technologies reduce discharges of compounds that are related to these chlorinated organic pollutants.

2.2 Source Identification:

Releases of UPOPs may occur from pulp and paper mills as by-product UPOPs such as PCDD and PCDF, or via the contamination of raw materials with PCB's or pesticides, via the following vectors:

- Emissions to air from burning of organic materials in the recovery cycle to generate energy and recover inorganic process chemicals;
- Emissions to air from burning wood and bark biomass to generate energy;
- **Emissions to water from pulp bleaching and preparation of bleaching chemicals, are the major sources of UPOP emissions from the industry;**
- Emissions to water from recycled fibre processing;
- Emissions to water from process chemical raw materials manufacture and contamination;
- Emissions / Transfer into pulp and de-inking sludges, from process water and final effluent treatments which may be applied on land, be incinerated or landfilled, and
- Emissions / Transfer into the products themselves (pulp or paper).

Looking at each of these in turn:

2.2.1 Emissions to air from burning of organic materials in the recovery cycle to generate energy and recover inorganic process chemicals.

With any such combustion process feedstock, attention has to be paid in all cases to good combustion conditions in order to minimise the formation of UPOPs.

2.2.2 Emissions to air from burning wood and biomass to generate energy.

Coastal pulp and paper mills using saltwater transport modes for logs can generate dioxins and furans which are created through the burning of salt contaminated hogged fuel. The material is then used as boiler fuel to produce heat and electrical energy for the pulp and paper process.

Again, with any such combustion process feedstock, attention has to be paid in all cases to good combustion conditions in order to minimise the formation of UPOPs.

2.2.3 Emissions to water from pulp bleaching and preparation of bleaching chemicals.

The use of elemental chlorine or the use of chlorine dioxide and elemental chlorine mixtures can lead to the formation of dioxins and furans in the bleachery. See tables 1,2 and 3 and refer to the bleaching sequence nomenclature in the Glossary.

The bleaching process step is the major source of UPOPs by orders of magnitude.

Table 1. Examples of different cooking and bleaching sequences used in European mills.

Wood Type	Cooking Technique	Bleaching Sequence	kappa	CLO ₂ (kg/t)	AOX (kg/t)
Softwood	Conventional	D(EOP)DED	30	95	2
Softwood	Conventional + Oxygen de-lignification.	D(EOP)DED	16	60	0.8
Softwood	Modified Cook + Oxygen de-lignification.	D(EOP)D(EP)D	10	30	0.3
Softwood	Conventional Cook + Oxygen de-lignification.	ZD	-	10	0.1
Softwood	Modified Cook + Oxygen de-lignification.	ZP	-	0	-
Hardwood	Conventional + Oxygen de-lignification.	D(EO)DED	13	40	0.5
Hardwood	Modified Cook + Oxygen de-lignification	D(EOP)DED	10	30	0.3
Hardwood	Conventional + Oxygen de-lignification.	ZD	-	5	0.1
Hardwood	Modified Cook + Oxygen de-lignification.	ZP	-	0	-

[EA S6.01, 2000]

Table 2. AOX and higher Chlorinated Phenolics produced in Bleaching of Wood pulps

Bleaching Sequence	AOX (kg/Adt of pulp)	Higher (3-5) chlorinated phenolics (g/Adt of pulp)
Chlorine based	8 – 9	80 - 100
Oxygen de-lignification followed by 50% substitution of chlorine by chlorine dioxide.	1.5 – 2	5 - 10
Oxygen de-lignification followed by 100% substitution (i.e. ECF bleaching)	<1	<2
Totally chlorine free (TCF) bleaching	0.005	-

[EA S6.01, 2000]

Table 3. AOX produced in Nonwood pulps (Straw and Bagasse)

Bleaching Sequence	Kappa	Charge Active Chlorine kg/odt	Brightness % ISO	Intrinsic Viscosity dm ³ /kg	COD kg/odt	AOX kg/odt
CEH	19	52	83	750	62	5.2
OCEH	11	25	86	800	38	2.8
(D+C)(EO)D	19	60	88	1000	74	1.8
O(D+C)(EO)D	11	32	89	900	40	0.7

90% ClO₂, substitution in (D+C). Non-wood Fiber Technology, Sunds Defibrator, Sundsvall, Sweden, 1999

2.2.4 Emissions to water from recycled fibre processing.

The use of recycled fibre introduces contamination UPOPs contained in the fibre supply. These travel through the process or are concentrated in the process sludges if de-inking is applied.

2.2.5 Emissions to water from process chemical raw materials manufacture and contamination.

The contamination of materials such as defoamers and wet strength agents with dioxin precursors.

2.2.6 Emissions into pulp and de-inking sludges, from process water and final effluent treatment sludges which may be applied on land, be incinerated or landfilled.

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There is also the potential for minor emissions from process chemicals and the products themselves (pulp or paper). The final paper products may contain UPOPs and other chlorinated organic contaminants from elemental chlorine bleaching, chemical usage on the papermachine from use of bleaches, biocides, slimicides, chlorinated wet end additives etc.

3 Primary and Secondary Measures

3.1 Best Available Techniques and Best Environmental Practices

The high degree of process-integration in the pulp and paper industry implies that the concepts of overall process BAT for all emissions must be related not only to separate processes, systems or lines, but whole installations must be examined and dealt with as entities.

The application of BAT will always need to be decided at local level, to take into account local circumstance and it can not be prescriptive in relation to individual process steps, giving only higher level descriptions on for example pre bleaching kappa reduction; the use of different bleaching chemicals and the available process steps to achieve reductions.

The BAT is stated in the following general guidance but no individual method is prescribed in the technical guidance table.

BAT only applies to new sources and substantially modified ones and so most of the approach taken in the guidance mostly reflects BEP for existing sources.

3.2 General Guidelines:

There are now severe restrictions on the discharges of chlorinated organics measured as AOX into the aquatic environment in many countries. Reductions of AOX can be achieved by a combination of several measures. The reduction of the kappa number ahead of the bleachery to reduce the bleaching effort needed and the substitution and replacement of molecular chlorine by chlorine dioxide or by oxygen bleaching chemicals. The reduction in the chloride content of effluents also makes it possible to further close up mill systems and recycle bleachery effluents back to the chemical recovery system which reduces emissions to water.

Lignin removal in the cooking stage is more advantageous than bleaching both economically and environmentally. The reduction of both chlorinated and non-chlorinated organic substances in the effluents of pulp mills can therefore be achieved to a large extent by in-process measures as for instance: increased delignification before the bleach plant; by extended or modified cooking and additional oxygen stages and efficient washing to reduce carry over to the bleach plant.

Further contributing factors that will decrease the emissions of AOX and other non-chlorinated toxic organic compounds into receiving waters, are the installation of end of pipe abatement measures such as effective external treatment plants of different designs.

In some parts of the world the trend within the industry is toward increased closure of the bleach plants either by using ECF (Elemental Chlorine Free) or TCF (Totally Chlorine Free) bleaching of pulps and the increased reuse of treated process waters by implementing production-integrated advanced wastewater treatment systems.

In summary the main steps outlined here are as follows:

- to adopt effective management techniques for the operation of an installation; BAT;
- to adopt a cooking method and recovery system that is amenable to low environmental impact bleaching regimes for the fibre types and satisfies the product requirements. BAT;

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- to promote the degree of delignification in cooking processes via:
 - chip handling and preparation
 - use of cooking catalysts,
 - extended (modified) cooking, Kraft BAT
 - extended cooking, Sulphite BAT
 - hot alkali extraction,;

- to reduce the carry over of lignin degradation products to the bleaching process by effective brown stock washing and screening processes; BAT
 - closed screening,
 - use of low precursor defoamers,
 - efficient washing

- to continue the delignification process using oxygen techniques; BAT;
- to use pre treatments to enhance bleaching effects, where applicable;
 - enzyme pretreatment,
 - hexenuronic acid removal,

- to reduce the chlorine multiple applied;
- to use oxygen reinforced with peroxide in an alkaline extraction stage;
- to increase substitution of chlorine with chlorine dioxide;
- to substitute chlorine with chlorine dioxide; BAT;
- to use chlorine dioxide generation methods with low by-product chlorine; BAT;
- to reduce use of chlorine compounds by the introduction of oxygen chemical bleaching; BAT;
- to use effective biological effluent treatment; BAT;
- to control sludge disposal.

The techniques or combinations of techniques which influence the emissions of UPOPs are detailed below.

3.2.1 General Measures for Management

In the absence of the BAT/BEP general guidance (which is in preparation) the following general measures are suggested:

1. Substitution. The identification and substitution of potentially harmful substances with less harmful alternatives. Use of a detailed inventory of raw materials used, chemical composition, quantities, fate and environmental impact.
2. Investment planning / cycles, co-ordination of process improvements to reduce technical bottleneck delays to the introduction of better techniques.
3. Training, education and motivation of personnel. 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.
4. Process control monitoring and optimisation. To be able to reduce different pollutants simultaneously and to maintain low emissions, improved process control is required. Raw materials specification and monitoring of raw materials for precursor materials.
5. Adequate maintenance. To maintain the efficiency of the process and the associated abatement techniques at a high level, sufficient maintenance has to be ensured.

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6. Environmental management system. A 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. Incorporation of environmental issues in process change controls. N.B ISO 14000 systems do not automatically cover environmental reporting.
7. Development of environmental monitoring and standard monitoring protocols.
8. Emissions monitoring for new facilities. Demonstrate performance of combustion processes and emissions to water.

3.2.2 Summary of Specific Measures

The measures and techniques that are available are summarised below with further more detailed information on each of these contained in Appendix 1.

SPECIFIC MEASURES AND TECHNIQUES			
Area	Measure	Primary	Secondary
Chemical Pulping Process selection.	Process amenable to low environmental impact acceptable bleaching regimes.	1. Fibre type pulping process selection to achieve a lower environmental impact in bleaching.	
Chemical Pulping Reduce effluent load of bleachery.	Reduce kappa via efficient cooking.	2. Optimum raw fibre materials handling and preparation. 3. Use of cooking catalysts.	
Chemical Pulping Reduce effluent load of bleachery.	Reduce kappa number via extended delignification.	4. Extended (modified) cooking - Batch digestion. 5. Extended (modified) cooking - Continuous digestion. 6. Sulphite pulping options. 7. Hot alkali extraction.	
Chemical Pulping Reduce effluent load of bleachery.	Reduce carry over to bleaching via efficient washing.	8. Efficient brown stock washing and closed screening. 9. Eliminate synthetic dioxin precursors.	
Chemical Pulping Reduce effluent load of bleachery.	Reduce kappa number via oxygen delignification.	10. Oxygen delignification.- non wood fibres. 11. Oxygen delignification – wood fibres.	
Chemical Pulping Reduce effluent load of bleachery.	Reduce kappa number via other pre bleaching treatments.	12. Pre bleach - Enzyme pre treatment. 13. Pre bleach treatments - Acid hydrolysis.	
Bleaching Reduce effluent load of bleachery.	Increase substitution and replace chlorine and hypochlorite with chlorine dioxide.	14. Chlorine optimisation and chlorine dioxide substitution. 15. Chlorine manufacture and handling. 16 + 17. ECF Bleaching. 18. Chlorine dioxide manufacture.	
Bleaching Reduce effluent load of bleachery.	Enhance lignin removal before chlorine dioxide stage.	19. Reinforced alkaline extraction.	
Bleaching Reduce effluent load of bleachery.	Use of ECF and TCF bleaching.	20. Acid chelation. 21. Increase bleach plant closure. 22. De-bottlenecking recovery boiler. 23. De-bottlenecking chlorine dioxide manufacture. 24. TCF bleaching. 25. Hydrogen Peroxide. 26. Ozone. 27. TCF Sequences (Existing plant). 28. TCF Sequences (Using Peroxide) 29. TCF Sequence (Peroxide and Ozone). 30. TCF Sequences (Ozone and Reinforced Peroxide).	
Effluent treatment Reduce emissions to water.	Treat effluents to degrade organics; adsorb persistent organics onto sludge.		31. Primary and biological treatments. 32. Spill Control.
Recovery Combustion processes.	Combustion control.		33. De inking sludge management. 34. Recovery boiler. 35. Sludge combustion. 36. Auxiliary boilers / bark boilers.

Others			37. Transport. 38. Fibre selection and storage. 39. Effluent treatment sludge management. 40. Combustion flue dust management.
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4 Performance Standards

Existing sub-national, national and supra-national limits applied to mills are detailed in Appendix 2.

The following table summarises this information as it is applied to **EXISTING** and **NEW** bleached kraft pulp mills:

4.1 Existing Plant

Country	AOX kg/ADt	PCDD / PCDF ng/m ³ To Water	PCDD / PCDF ng/m ³ To Air	Defoamers DBD and DBF ppb
EU	0.40 and 0.25 ¹	*	0.1 ²	
New Zealand	0.34			
Canada - Federal	None	Zero	0.5	10 and 40
Canada (British Columbia)	0.6 (sulphite 1.0)			
USA	0.951 / 0.623 / (0.512) ³	M.L. ⁴ / 31.9		
Brazil	0.2 - 1.0			
World Bank	0.4			

4.2 New Plant

Country	AOX kg/Adt	PCDD / PCDF ng/m ³ To Water	PCDD / PCDF ng/m ³ To Air	Defoamers DBD and DBF ppb
EU	0.40 and 0.25 ⁵	-	0.1 ²	
New Zealand	-			
Canada - Federal	None	Zero	0.1	10 and 40
Canada (British Columbia)	0.6 (sulphite 1.0)			
USA	0.476 / 0.272 / (0.208) ³	M.L. ⁴ / 31.9		
Brazil	-			
World Bank	0.2			

1. After Primary and after biological treatments respectively (Comply by 2007).
2. CEN method (EN 1948, 1997) sample period 4 hour minimum 8 hour maximum.
3. Daily maximum and monthly average for continuous discharges. New plant limit of 0.208 kg/metric tonne and existing plant limit of 0.512 kg/ metric tonne yearly average for non continuous discharges (final effluent).
4. ML means less than the minimum level at which the analytical system gives recognizable signals and an acceptable calibration point and refers to bleach plant effluent. Monthly maximum.
5. After Primary and after biological treatments respectively.

Further details, including monitoring periods and methods are given in Appendix 2.

Performance standards and compliance periods are recommended as follows:

Type	Media	Compliance by	Emission Limit Value	Comment
Existing	Air PCDD/PCDF	Within 10 years	0.1 ng/m ³ I -TEQ	From EU and Canadian limits
Existing	Water PCDD/PCDF	Within 10 years	< M.L / 31.9	From USA limits
Existing	Water AOX	Within 10 years	0.25 kg/ADt	From EU limit
New	Air PCDD/PCDF	Entry into force	0.1 ng/m ³ I -TEQ	From EU and Canadian limits
New	Water PCDD/PCDF	Entry into force	< M.L / 31.9	From USA limits
New	Water AOX	Entry into force	0.25 kg/ADt	From EU limit

Additional dioxin precursor limits on defoamers would also be advantageous (see the Canadian limits on DBD and DBF above).

5 Performance Reporting

Performance reporting is recommended as follows:

For dioxin and furan emissions to air from combustion of process derived materials - an annual isokinetic emission testing period. Annual emission testing could be reduced in frequency or suspended once emissions are shown to be satisfactory on a continued and constant basis.

For dioxin and furan emissions to water – a monthly testing period. A mill may adopt quarterly sampling if it has had no measurable concentrations in its last three consecutive monthly samples, a mill may adopt annual sampling if it has had no measurable concentrations in its last three consecutive quarterly samples. The testing period reverts back to monthly testing if either a quarterly test or an annual test detects dioxins or furans. Treatment sludges used for agricultural benefit may also need to be tested before use.

Where emissions testing is not possible (e.g., analytical capacity is not readily available), the use of PCDD/PCDF emission factors associated with a similar mill type and operation is suggested as an interim performance reporting requirement until such time as annual emissions testing and analysis is available. Emission factors for releases of PCDD/PCDF from mills are presented at page 184 in the UNEP Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases, May 2003 (URL:www.pops.int).

The commonality of this issue across all sector guides would indicate that it needs to be covered as a separate report and draw on the information on standards and testing methods contained in each of the individual sector guides.

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DEFINITIONS

ADt	Air dried tonne of paper (paper contains around 7% water under ambient conditions)
AOX	Adsorbable Organic Halogen
APP	Alkaline peroxide process
BAT	Best Available Techniques
Bleaching Sequence letters :	
C	is elemental chlorine Cl ₂
E	is alkaline extraction NaOH
H	is hypochlorite
D	is chlorine dioxide ClO ₂
(CD)	is mixtures of chlorine and chlorine dioxide
O	is oxygen
(EO)	is alkaline extraction with oxygen
P	is hydrogen peroxide
(EOP)	is alkaline extraction with oxygen and hydrogen peroxide
aP	is hydrogen peroxide in acidic conditions
(PO)	is peroxide pressurised with oxygen
(DN)	is chlorine dioxide with subsequent neutralisation
Z	is ozone
Paa	is peracetic acid
Ca	is Caro's acid (sulphuric acid and hydrogen peroxide)
Pxa	is mixed peracids
Q	is chelation stage
X	is enzyme treatment
BOD	Biochemical Oxygen Demand
Broke	Paper made on the paper machine and returned to the process usually because of web breaks
CHP	Combined heat and paper plant
COD	Chemical Oxygen Demand
CTMP	Chemi-thermo-mechanical-pulping processes (using sulphite or APP)
DAF	Dissolved air flotation
DTPA	Diethylene triamino pentaacetic acid
ECF	Elemental chlorine free (pulp bleached without elemental chlorine)
EDTA	Ethylene diamine tetra-acetic acid
EMS	Environmental Management System
ETP	Effluent treatment plant
Kappa No	The Kappa number is an indirect measure of the residual lignin content in a pulp measured via the consumption of an oxidant chemical (e.g potassium permanganate). Measure used for process control.
Integrated-mill	A mill in which both pulping and paper-making take place
ITEQ	International Toxicity Equivalents
NTA	Nitrilo triacetic acid
PCDD	Polychlorinated dibenzo-p-dioxins
PCDF	Polychlorinated dibenzofurans
PAE	Polyamidoamine-epichlorhydrin resins
PAM	Polyacrylamides
PCDD	Poly chlorinated dibenzo dioxins
PCDF	Poly chlorinated dibenzo furans
PCP	Pentachlorophenol
PEI	Polyethyleneimines
RCF	Recycled fibre
STW	Sewage treatment works
TCDD	2,3,7,8 –tetrachloro-p-dibenzodioxin
TCDF	2,3,7,8 – tetrachloro dibenzofuran
TCF	Totally chlorine free (pulp bleached without any chlorine compounds)
TOC	Total Organic Carbon
VOC	Volatile organic compounds
Wood-free	Paper made from pulp from which the lignin has been largely dissolved by chemical means

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The table below expands on each of these techniques:

Management Options	Release Characteristics	Applicability	Other Considerations
Chemical Pulping Primary Measures –			
1. Process Selection	Fibre type pulping process selection to achieve a lower environmental impact in bleaching.	The cooking method and any associated recovery plant should be chosen, to be amenable to low environmental impact acceptable bleaching regimes as well as to minimise releases to air and water in general.	
2. Optimum Fibre Raw Materials Handling. Attention to optimisation of materials handling and chipping performance to obtain even and efficient cooking. Take all necessary upstream measures to reduce the negative effects on fibres caused by storage, seasoning, contamination / cleaning, poor chip dimensional controls, screening and feeding of fibres depending on fibre type and pulping process.	Maximisation of a specific pulping process' performance avoidance of over and under treatment. Reduction of kappa via efficient cooking ahead of the bleachery to reduce bleaching chemical consumption. Raw material storage, seasoning periods, chipping processes, chip storage and chip dimensions all affect cooking liquor penetration speeds. Yield losses and gains (process specific) are caused by extended storage. The form of fibre storage affects the degradation process also. Pulp strengths are also affected. Bark contamination and chip damage critical in most sulphite wood pulping. Chip dimensions critical in kraft wood pulping.	All pulping processes. Generally cheap measures applied upstream of pulping process. Bamboo is crushed to break up the nodes (which are resistant to pulping), and then chipped like wood. Abaca, flax and hemp - Stock preparation involves pre-cutting, to reduce the excessive fibre length. Bagasse - pith is removed during an initial de-pithing stage, to avoid greater chemical consumption during cooking.	
3. Use of Cooking Catalysts. Polysulphide and Anthraquinone kraft modifications	Reduction of kappa via efficient cooking ahead of the bleachery to reduce bleaching chemical consumption. Alkaline polysulphide / sulphur addition or oxidation of sulphide 1.5 to 2.0% yield gain at same kappa. AQ stabilises carbohydrates, doses 0.5 to 0.1 kg/t wood increases yield or allows cooking to lower kappa (2% to 3.0% yield increase at same kappa (on dry wood)). [PMS&T FAPET, Series, 1999]	Kraft and soda pulping. Increased pulp yields in comparison to conventional kraft cooking and can facilitate the use of extended delignification methods in mills with limited recovery boiler capacity. Polysulphide or polysulphide-anthraquinone (AQ) cooking can also be used to reduce pulp lignin content at a given pulp yield, thereby reducing the load on the bleach plant, bleaching chemical requirements, and AOX in bleach plant effluents. Payback periods of less than 1 year were estimated assuming a 2% increase in pulp yields (polysulphide only).	Polysulphide and AQ effects are additive / synergistic.
4. Delignification via Extended (Modified) Cooking - BATCH Pulp entering the bleach plant with low kappa number requires less bleaching chemicals and thus pollution load from the bleaching plant (among others chlorinated organic compounds where chlorine is	Reduction of kappa ahead of bleachery to reduce bleaching chemical consumption. Conventional cooking has maximum achievable limits of kappa 30 – 32 for softwoods and 18-20 for hardwoods. Modified cooking kappa number reductions have been accomplished without loss of strength properties. Kappa reduction to 18 – 22 for softwoods and 14-16 for hardwoods. [EA S6.01, 2000] RDH and Superbatch - In batch cooking, extended	Kraft batch processes. Extended modified cooking and oxygen delignification should be considered as a unit because what is essential from an environmental point of view is the total degree of delignification achieved as a result of delignification in the stages before the pulp enters to the bleach plant. The process can be installed as a retrofit in conventional plants if the digester capacity is large enough. In practice, the modifications of an existing batch cooking system can be done	Commercially available. Proven wood based technologies. All these displacement cooking processes show a substantial energy saving and an improved pulp quality. BOD- and COD-reduction also if the washing efficiency is increased as well. (Additional 2-4 MEuros for a 1500 ADT/day mill). . [EIPPCB BREF, 2001]

Management Options	Release Characteristics	Applicability	Other Considerations
<p>used) will decrease. Lignin reductions of 40 to 60% over conventional cooks.</p> <p>Increase delignification before the bleach plant via extended modified cooking – BATCH</p> <p>Rapid Displacement Heating (RDH), SuperBatch and EnerBatch techniques.</p>	<p>delignification is carried out by means of displacement and black liquor recycling techniques. Pretreatment (impregnation) with black liquor is carried out in order to decrease the heat consumption and at the same time to increase the initial sulphide concentration and decrease the effective alkali charge.</p> <p>Enerbatch - Pretreatment with white liquor followed by a pretreatment with black liquor.</p>	<p>with additional batch digesters and additional investment costs without losing the capacity of the cooking plant</p> <p>Generally, the impact of extended cooking on production is very site specific. If the chemical recovery system is a bottleneck at a mill then introduction of extended delignification risks a loss in production due to the increased demand on that part of the system.</p> <p>The measure can be adopted in new kraft mills and to a limited extent in existing mills.</p> <p>1500 Adt/day mill 4-5 Meuros. [EIPPCB BREF, 2001]</p>	<p>Kappa reduction should be compared to the possible loss of yield and increased wood consumption.</p>
<p>5. Delignification via Extended (Modified) Cooking - CONTINUOUS</p> <p>Pulp entering the bleach plant with a low kappa number requires less bleaching chemicals and thus pollution load from the bleaching plant (among others chlorinated organic compounds where chlorine is used) will decrease. Lignin reductions of 40 to 60% over conventional cooks.</p> <p>Increase delignification before the bleach plant via extended modified cooking – CONTINUOUS</p> <p>Modified Continuous Cook (MCC) and Isothermal Cooking (ITC). And Andritz - Extended Modified Continuous Cook (EMCC), LoSolids and Enhanced Alkali Profiled Cooking) EAPC.</p>	<p>Reduction of kappa ahead of bleachery to reduce bleaching chemical consumption.</p> <p>Modified cooking kappa number reductions have been accomplished without loss of strength properties.</p> <p>ITC and MCC retrofits have achieved kappa reduction to 20 - 24 for softwoods and 14-18 for hardwoods. [EA S6.01, 2000]</p> <p>The techniques decrease the initial alkali concentration, keep an even concentration of alkali during the cooking process and a low concentration of the dissolved lignin in the final part of the cook. White liquor is also charged to the washing zone in order to extend further the delignification in the digester in EMCC. In ITC the whole digester vessel is used for delignification which means lower cooking temperature is used.</p> <p>With large digesters at new installations it is possible to obtain kappa 15 – 16 for softwoods and 12 for hardwoods.</p>	<p>Retrofits to kraft batch and continuous or (Kamyrr) processes.</p> <p>Extended modified cooking and oxygen delignification should be considered as a unit because what is essential from an environmental point of view is the total degree of delignification achieved as a result of delignification in the stages before the pulp enters to the bleach plant.</p> <p>A number of continuous digesters have been retrofitted to ITC without having to sacrifice production (where digesters are large enough). 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).</p> <p>Generally, the impact of extended cooking on production is very site specific. If the chemical recovery system is a bottleneck at a mill then introduction of extended delignification risks a loss in production due to the increased demand on that part of the system.</p> <p>1500 Adt/day mill 4-5 Meuros. [EIPPCB BREF, 2001]</p>	<p>Commercially available. Proven wood based technologies.</p> <p>All these displacement cooking processes show a substantial energy saving and an improved pulp quality.</p> <p>The measure can be adopted in new kraft mills and to a limited extent in existing mills.</p> <p>BOD- and COD-reduction also if the washing efficiency is increased as well. (Additional 2-4 MEuros for a 1500 ADT/day mill). [EIPPCB BREF, 2001]</p> <p>ITC retrofit at constant production capacity does not require additional washing capacity. ITC does not increase steam requirements.</p> <p>Kappa reduction should be compared to the possible loss of yield and increased wood consumption.</p>
<p>6. Sulphite Pulping Options.</p> <p>Two stage cooking.</p>	<p>Reduction of kappa ahead of bleachery to reduce bleaching chemical consumption.</p> <p>Two stage cooking where pH is altered in second stage gives higher yield in magnesium and sodium sulphite cooking processes. Cooking can be brought down to below kappa 10. Cooking can be extended further to produce speciality pulps. See Oxygen delignification also.</p>	<p>Sulphite pulping.</p> <p>Magnesium and sodium based pulping also allows recovery.</p>	<p>Yield increase is at the expense of strength.</p>
<p>7. Hot Alkali Extraction</p>	<p>Increases lignin removal by leaching before resorption can occur in the washing stage.</p>	<p>All alkaline pulping.</p>	<p>The effect of hot alkali extraction is additive to that of oxygen delignification.</p>

Management Options	Release Characteristics	Applicability	Other Considerations
Hot alkaline leaching after cooking. Effective removal of the cooking degradation products.	Reduces kappa number. [PMS&T Vol 6, FAPET 1999]		More selective than extended cooking.
<p>8. Efficient Brown Stock Washing and Screening Closure</p> <p>Brown stock screening plant can be completely closed.</p>	<p>Carry over or washing losses to the bleach plant increases bleaching chemical consumption.</p> <p>Thorough washing can reduce the lignin content of the pulp before bleaching. Any dissolved lignin in the water associated with it will increase the bleaching requirement.</p> <p>Use wash presses, diffuser and displacement washers.</p> <p>Carbon dioxide addition can improve the washing effect. [EA S6.01, 2000]</p> <p>Better cooking technology / efficiency reduces shives and knots so closed screening can be accomplished which contributes to the reduction of organic compounds in the effluents. The organics can then be recovered in the recovery boiler. Washing losses (expressed in terms of COD) can be reduced by 50%.</p>	<p>Closed screening is reality in most European mills.</p> <p>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. Higher pulp consistencies can now be screened. Consequences are lower investment costs and consumption of electrical energy.</p> <p>Bottleneck issue for evaporation capacity.</p> <p>1500 ADT/d mill - 4-6 MEuros (new mills), 6-8 MEuros (existing mills). Operating costs 0.3-0.5 MEuros / year. [EIPPCB BREF, 2001]</p>	<p>Non wood slow drainage characteristics mean larger washer units are required. [AGIC, 1990]</p> <p>Current non wood water use per tonne of product can be very high.</p>
<p>9. Elimination of Synthetic Dioxin Precursors</p> <p>Use low precursor defoamer additives (clean defoamers).</p> <p>Spills should be guarded against by means of a suitably engineered handling system.</p> <p>Care in defoamer selection. Degree of chlorine substitution and other measures applied needs to be taken into account.</p>	<p>Dioxin and/or dioxin precursors have been discovered in pentachlorophenol contaminated wood, paint, defoamers, cutting oils, and other inadvertent inputs to pulp-making. The precursors are easily chlorinated in chlorine based bleaching, to yield dioxin among other compounds. Strict control is necessary for complete elimination.</p> <p>De-foamers are a wide range of chemicals used to prevent foaming and to destroy produced foam respectively. Pulp and paper mills use defoamer additives such as oils with high aromatic content that, in the presence of a chlorine bleaching process, could be a source of dioxins and furans in mill products and in their effluents. To manufacture these defoamers, oils and polymers are used that can contain dibenzo-para-dioxins and dibenzofurans. These can react with chlorine to form dioxins and furans.</p> <p>Spills can suppress bubble formation and the aeration mechanism in aerobic effluent plants.</p>	<p>General applicability to non TCF bleaching.</p>	<p>Defoamers: Often lipophilic and are likely to bioaccumulate. Possible treatment plant effects. Inefficient effluent treatment plant operation will reduce treatment of other contaminants.</p> <p>Oil free polyol esters or silocon based defoamer products are available..</p> <p>Mineral oil based amide or silica products which are precursor free are also available.</p> <p>Canadian mills are already subject to CEPA D/F defoamer regulations prohibiting purchase of such products) [CEPA Regulations (SOR/92-268) , 1992]</p>
<p>10. Oxygen delignification</p>	<p>The major benefits of oxygen delignification are the decrease in the amount of chemicals needed in final bleaching and total costs for bleaching chemicals and a decrease of pollution load from the bleaching plant</p>	<p>Oxygen delignification has the same potential for environmental improvement in the non-wood fibre area as it has in the wood based fibre industry.</p>	<p>The reduction of kappa, organic substances and the consumption of chemicals in oxygen delignification are strongly related to the efficiency of washing between stages.</p>

Management Options	Release Characteristics	Applicability	Other Considerations
<p>Nonwood pulps</p> <p>Increase delignification before the bleach plant.</p> <p>Medium consistency is more selective and has lower investment costs.</p>	<p>(COD and chlorinated organic compounds from final bleaching in case of non TCF bleaching).</p> <p>About 50% of the remaining lignin in the brown stock can be removed.</p> <p>For non-wood fibres like bagasse and straw it is possible to reduce the kappa number before bleaching down to 8-10 while preserving yield and fibre quality.</p> <p>Addition of an oxygen stage to existing bleacheries reduces bleach chemical consumption by 50% i.e. (O) CEH</p>	<p>Can be applied at sulphite mills also.</p> <p>Medium consistency mixer technology now proven (high shear mixers) Because of better selectivity and lower investment costs the Medium Consistency (MC, 10-15%) system has dominated mill installations in the 1990's. [EIPPCB BREF, 2001]</p>	<p>Many mills still discharge the effluent from oxygen elignification directly into the effluent treatment plant instead of recovering it.</p> <p>The recycling of oxygen-stage effluent to the recovery system by way of the brownstock washers is possible.</p>
<p>11. Oxygen De-lignification</p> <p>Wood pulps</p> <p>Increase De-lignification before the bleach plant.</p> <p>Medium consistency is more selective and has lower investment costs.</p>	<p>The major benefits of oxygen De-lignification are the decrease in the amount of chemicals needed in final bleaching and total costs for bleaching chemicals and decrease of pollution load from the bleaching plant (COD and chlorinated organic compounds from final bleaching in case of non TCF bleaching). Chlorine gas bleaching can be reduced by 40 to 50% by oxygen De-lignification.</p> <p>Much of the remaining lignin in the brown stock can be removed and recovered by adding oxygen to an alkaline fibre suspension. The oxygen De-lignification takes place in one or two stages after the cooking and prior to the bleaching and can achieve a further De-lignification efficiency of 40 to 60%. An efficiency of up to 70% normally requires two-stage installations.⁴ Conventional cook and oxygen de-lignification can achieve kappa 18-22 softwoods, and kappa 13-15 for hardwoods. Extended cooking and oxygen de-lignification can achieve kappa 8-12 depending on wood species. [EA S6.01, 2000]</p> <p>The waste liquor can be sent counter-currently to the chemical recovery system. Normally uses the oxidised cooking liquor, to maintain sodium balance. Magnesium sulphate can be added to preserve strength.</p> <p>Up to 60% AOX reduction when used with extended cooking [EA S6.01, 2000]</p>	<p>Modern kraft mills are always designed for a combination of modified cooking and oxygen de-lignification and for the effect on the environment (discharges of COD and AOX) both techniques have to be considered together.</p> <p>Can be applied at sulphite mills also.</p> <p>Medium consistency mixer technology now proven (high shear mixers). Because of better selectivity and lower investment costs the Medium Consistency (MC, 10-15%) system has dominated mill installations in the 1990's. [EIPPCB BREF, 2001]</p> <p>1500 ADT/d 35 – 40 MEuros, 2.5 – 3.0 MEuros operating costs. [EIPPCB BREF, 2001]</p>	<p>The installation of oxygen de-lignification phase in the existing kraft mill may decrease the fibre line production if de-lignification effluents are recovered and there is not enough spare capacity in the whole recovery system.</p> <p>Additional steam requirements.</p> <p>The reduction of kappa, organic substances and the consumption of chemicals in oxygen de-lignification are strongly related to the efficiency of washing between stages. The mentioned environmental performance is not reached without efficient washing.</p> <p>The recycling of oxygen-stage effluent to the recovery system by way of the brown stock washers is possible because chemicals that do not contain sulphur are used.</p> <p>Many mills still discharge the effluent from oxygen de-lignification directly into the effluent treatment plant instead of recovering it.</p> <p>Additional dry solids loads require additional recovery capacity, generally 4 to 6% for the recover boiler and also 4 to 6% more capacity in lime recausticising..</p> <p>High consistency installations (HC, 25-30%) are in use also.</p>
<p>12. Enzyme Treatments</p> <p>Pre treatment via enzyme addition to pre bleach brown stock.</p>	<p>Reduction of kappa ahead of the bleachery to reduce bleaching chemical consumption. 15-25% savings in chlorine chemicals.</p> <p>Benefits have been demonstrated for enzymatic pre-treatment before chemical bleaching, for example with</p>		<p>Marginal kappa reduction, 1-2 units. Slight yield loss. Pulp quality unaffected.</p>

Management Options	Release Characteristics	Applicability	Other Considerations
	xylanases.		
<p>13. Acid hydrolysis for Hexenuronic Acid Removal</p> <p>A pre treatment after conventional kraft cooking to remove the hexenuronic acids (HexA) before bleaching of the pulp via ECF and ozone sequences.</p>	<p>Add an acid hydrolysis step before or after oxygen stage.</p> <p>Hexenuronic acid groups can be converted into furan derivatives (i.e., 2-furoic acid and 5-carboxy-2-furaldehyde), for example, prior to ECF and TCF bleaching by mild acid hydrolysis. This kind of treatment reduces the consumption of bleaching chemicals and the use of chelating agents.</p> <p>ECF - HexA reacts with chlorine dioxide and ozone.</p> <p>TCF- HexA does not react with oxygen or hydrogen peroxide.</p>	<p>Fibres with high xylan hemicellulose fibre content. Hardwoods and non woods.</p> <p>Not applicable to Soda, Soda AQ or polysulphide since HexA concentrations are low in these methods.</p> <p>Not applicable to TCF if using oxygen and peroxide bleaching. In the case of ozone bleaching, hexenuronic acid removal may save ozone.</p> <p>[VTT Biotechnology, 2003]</p>	
Primary Measures – Bleaching (See glossary for bleaching sequence nomenclature)			
<p>14. Chlorine Optimisation and Chlorine Dioxide Substitution</p> <p>Replace chlorine by chlorine dioxide in the first bleaching stage. With the goal of complete substitution of chlorine dioxide in the first stage of bleaching (independent of the extent of de-lignification of unbleached pulp).</p> <p>SHORT TERM: Where chlorine is in use for bleaching, then optimise chlorine use. Use low chlorine multiple bleaching (<0.15).</p> <p>Introduce chlorine dioxide Substitution in the first stages of bleaching (depending on kappa) to minimise formation of chlorinated organic.</p> <p>Avoid the use of de-foamers with high aromatic content.</p> <p>MEDIUM TERM: Increase level of substitution with chlorine dioxide.</p>	<p>Chlorine dissolves residual lignin by oxidation and chlorination, thus generating chlorinated organic. If the organic group is aromatic then chlorinated aromatics are produced. Elemental chlorine can be replaced by chlorine dioxide in the first bleaching stages, increasing the degree of substitution with chlorine dioxide decreases the formation of chlorinated organic and can virtually eliminate the formation of dioxins and furans</p> <p>Optimisation: Split addition. Use smaller multiple charges. Use low chlorine multiple bleaching (<0.15). Avoid chlorine dioxide substitution above a 0.15 chlorine multiple. Above 50% substitution gives lowest kappa in (DC)E sequences for soft and hardwoods. [USC, 1989]</p> <p>Ensure good mixing and process control.</p> <p>Reduce acidity before chlorine addition. (However see pH comments on chlorate formation when used with chlorine dioxide).</p> <p>High levels of Substitution: Dioxins and furans not detectable in bleach plant effluents above 85% chlorine dioxide substitution. [SYKE, No 17, 1996] (pH 4 is optimum). However, chlorine dioxide will still produce a small amount of elemental chlorine through reactions in the bleaching process. Chlorine produced in this way is then capable of chlorinating lignin breakdown products and other organic compounds. When elemental chlorine</p>	<p>General applicability.</p> <p>Non wood and Sulphite pulps may not require the use of chlorine containing bleaching chemicals.</p> <p>Increasing levels of substitution of chlorine by chlorine dioxide requires modifications to the bleaching plant and expansion of the chlorine dioxide manufacturing plant.</p> <p>A pressurised PO stage can be added to the end of an existing mill's bleach plant to enable ECF pulps to be produced without having to increase chlorine dioxide capacity.</p> <p>The investment costs for a 1500 Adt/d ECF bleaching plant are 8-10 MEuros at new mills and 3-5 MEuros at existing mills. The operating costs are 10-12 MEuros/a. These costs are based on the assumption that an existing bleach plant can be used and the investment costs include the necessary increase in chlorine dioxide production. The operating costs also contain the additional cost of using chlorine dioxide instead of elemental chlorine. [EIPPCB BREF, 2001]</p>	<p>Roughly 25% of the pulp produced world-wide is still bleached with elemental chlorine. The mills in western Europe have virtually stopped the use of molecular chlorine for bleaching of pulp.</p> <p>The chlorine charge is generally based on the so-called chlorine multiple or kappa factor, which is the ratio of chlorine charged (in % active chlorine on pulp) to the kappa number of incoming pulp.</p> <p>Chlorine dioxide dissolves lignin without formation of chlorinated organic and protects cellulose from degradation products. Whereas chlorine tends to substitute and combine with lignin, chlorine dioxide typically oxidises the lignin, opening up the aromatic structure. Any remaining chlorinated organic pollutants formed by ClO₂ bleaching are water soluble and do not bio-accumulate.</p> <p>A potential problem when ClO₂ is used is the formation of chlorate. It is important, when using chlorine dioxide for de-lignification, to manipulate reaction conditions to minimise the formation of chlorate and free chlorine or hypochlorous acid so as to improve de-lignification efficiency and minimise the formation of chlorinated organic matter. This implies that pH should be low when</p>

Management Options	Release Characteristics	Applicability	Other Considerations
<p>INVESTMENT CYCLE TERM: The Elimination of the use of elemental chlorine and hypochlorite, and move to ECF techniques (see below).</p>	<p>and hypochlorite is completely replaced by chlorine dioxide (100%), the process is known as Elemental Chlorine-Free (ECF). However, as noted above, this term is not entirely correct, for a small amount of elemental chlorine accompanies the use of chlorine dioxide. [CBNS, 1996]</p> <p>100% chlorine dioxide substitution is possible if combined with alkaline reinforced extraction stages (oxygen and peroxide). See below.</p> <p>Bleaching sequences:</p> <p>CEH (non woods) CEHD CEHDED (higher brightness) CEDED (CD)EDED With an oxygen de-lignification stage or reinforced extraction stage then: OCEH (non woods) (D+C)(EO)D (non woods) With oxygen de-lignification and reinforced extraction then: O(D+C)(EO)D (Non woods) O-(CD)EDED O-(CD)(EO)DED</p>		<p>chlorine dioxide is used in the first stage of bleaching.</p> <p>About 10% of ClO₂ as active chlorine shows up as chlorate. This means that about 4-6 kg of chlorate is formed per tonne of pulp at ECF-bleaching at kappa 18. Chlorate is toxic to bacteria and plankton at levels of about 3-4 mg/l. Therefore adequate effluent treatment is needed.</p> <p>For on site chlorine and sodium hydroxide production see the guidance on the chemicals industry.</p> <p>De-foamers are a major source of dioxin and furan precursors. De-foamer additives such as oils with high aromatic content that, in the presence of a chlorine bleaching process, could be a source of dioxins and furans in mill products and in their effluents. See De-foamers above.</p> <p>Sulphite pulps - Chlorine dioxide bleaching is no longer used in Europe, with most sulphite mills producing TCF pulps. Mostly oxygen, sodium hydroxide and hydrogen peroxide..</p> <p>The lignin content of hardwoods and some non wood fibre such as straw is lower than softwoods and so these pulps are easier to bleach by non chlorine methods.</p> <p>Some non wood chemimechanical pulps continue to be bleached with chlorine in some mills. [Deli PCB, 2003]</p>
<p>15. Chlorine Manufacture and Handling</p> <p>Integrated pulping and chlor-alkali installations are in use in some countries.</p> <p>For on site chlorine and sodium hydroxide production see the guidance for the chemical industry.</p>		<p>On site chlorine and sodium hydroxide production.</p> <p>Some remote, sufficiently large mills or mills with availability of suitably priced electric energy may produce their own chlorine, caustic soda, chlorate and oxygen.</p>	<p>Produced on-site or off-site together with sodium hydroxide by brine electrolysis.</p> <p>Chlorine gas handling.</p>
<p>16. ECF & TCF bleaching</p>	<p>The production of oxygen based bleaching chemicals requires less toxic precursors than does chlorine dioxide.</p>	<p>General applicability.</p>	<p>ECF effluents cannot currently be easily re-circulated to the chemical recovery cycle due to the build up of chloride.</p>

Management Options	Release Characteristics	Applicability	Other Considerations
<p>Conversion of mills to ECF or TCF reduces and virtually eliminates the production of persistent and bioaccumulative chlorinated compounds.</p> <p>In global terms, a greater reduction in emitted general AOX loads could be achieved if the remaining mills with chlorine bleaching were to change over to ECF bleaching than if the ECF pulp mills were to change over to TCF bleaching. [TU Darmstadt, 2002]</p>	<p>Some "ECF" labelled mills may still generate UPOPs in ECF bleaching because of high by-product or co-product chlorine. Chlorine dioxide bleaching also forms hypochlorous acid which can react directly with the aromatic rings on the lignin or be converted to elemental chlorine. [CBNS, 1996]</p> <p>There will also be chlorine gas present in manufactured chlorine dioxide depending on the generation method used. See Chlorine dioxide manufacture below.</p> <p>ECF bleaching without modified cooking and extended de-lignification will still give rise to higher AOX</p> <p>Provided the pulp has a low enough kappa number after extended cooking and oxygen de-lignification then TCF bleaching with peroxide and ozone can be carried out.</p>		<p>TCF alkaline bleaching effluents can go to the recovery cycle (subject to non process element control / removal). TCF closure – reduces effluent loads to water (including non UPOP non-chlorinated toxic compounds in general).</p> <p>The elimination of chlorine chemicals improves hazard profiles in the work environment and reduces the danger of chemical spills when they do occur.</p> <p>ECF pulp bleached with chlorine dioxide accounts for the predominant share of roughly two-thirds of the bleached pulp produced world-wide. TCF pulp only accounts for around 7% and is primarily produced in mills in Northern and Central Europe. [TU Darmstadt, 2002]</p> <p>ECF and TCF process environments are less corrosive than traditional bleaching processes such as chlorine or hypochlorite due to reduced chloride ion concentration.</p> <p>ECF and TCF produce specific pulp products. TCF pulps have lower strength properties than chlorine and ECF bleached pulps. This can be compensated for by lower brightness if this is acceptable. TCF product quality does not therefore meet all ECF product users' required pulp properties.</p> <p>Specific TCF product markets are, however, developing fast due to consumer demand and the supply chain effect of specifying paper products based specifically on TCF pulps.</p>
<p>17. Elemental Chlorine Free (ECF) Bleaching (chlorate reduced)</p> <p>Elemental Chlorine Free (ECF) bleaching is a sequence without the use of elemental chlorine made possible by low initial kappa.</p> <p>In ECF, chlorine dioxide is usually the main bleaching agent.</p>	<p>The complete elimination of dioxins and furans depends on the kappa number and the purity of the chlorine dioxide supply. With high kappa and impure chlorine dioxide the probability of dioxin formation increases. Impure chlorine dioxide (elemental chlorine can be up to 9% with some generation methods). [EIPPCB BREF, 2001]</p> <p>Chlorine is still formed in chlorine dioxide bleaching during bleaching reactions and will produce organochlorine compounds. These quantities are, small however compared with what is formed in chlorine gas chlorination.</p>	<p>General applicability.</p> <p>The label of Elemental Chlorine Free - ECF - has been used for processes involving a wide range of chlorine (by-product or co-product) in chlorine dioxide. Up to 0.9 tonnes of chlorine per tonne of chlorine dioxide can be present depending upon the chemical production route selected to produce the chlorine dioxide.</p> <p>"ECF Light" can be applied to both softwoods and hardwoods.</p> <p>Reinforced alkaline extraction EO and EOP are more extensively used than in chlorine bleaching.</p>	<p>However, the complete elimination of PCDD/PCDF in ECF bleached effluents depends on the kappa number and the purity of ClO₂. With high kappa and impure ClO₂ the probability of forming PCDD/PCDF increase.</p> <p>In 1998 54% of the world market was supplied by ECF pulp.</p>

Management Options	Release Characteristics	Applicability	Other Considerations
<p>"ECF Light" sequences meaning bleaching sequences in which chlorine dioxide consumption is low are also in use. The use of ozone (DZ) and peroxide (PO) stages can reduced the formation of chloro-organic compounds considerably.</p>	<p>Bleaching sequence evolutions: With oxygen de-lignification and reinforced extraction (see Reinforced Alkaline Extraction above):</p> <p>O-DEDED O-D(EO)DED O-D(EO)(DN)D O-D(EOP)DD O-D(DN)(EOP)D</p> <p>"ECF Light" sequence examples: D(EO)Q(PO) (DZ)(EO)DED (DZ)(EOP)D (DZ)(EO)Q(PO).</p>	<p>The investment costs for a 1500 Adt/d ECF bleaching plant are 8-10 MEuros at new mills and 3-5 MEuros at existing mills. The operating costs are 10-12 MEuros/a. 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 the additional cost of using chlorine dioxide instead of elementary chlorine. [EIPPCB BREF, 2001]</p>	
<p>18. Chlorine Dioxide Manufacture</p> <p>Use Mathieson or R8 chlorine dioxide manufacturing methods.</p>	<p>Chlorine dioxide is produced on-site from sodium chlorate, chlorine gas may be evolved depending on production method.</p> <p>Small quantities 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 the chlorine dioxide is used in bleaching.</p> <p>Impure chlorine dioxide leads to dioxin and furan formation.</p> <p>Bleachery changes (more chlorine dioxide use for example) will impact on generation capacity requirements. The quantity applied can increase from low levels used in chlorine dioxide carbohydrate protection through higher levels of chlorine substitution. The issue of generation capacity and de bottle-necking is therefore important here.</p>	<p>Chlorine / chlorine dioxide and ECF bleaching.</p>	<p>The intake of sulphur to the inorganic chemical balance when operating with a high proportion of chlorine dioxide in bleaching means a high amount of sulphur may have to be discharged or disposed as neutral salts (e.g. Na2SO4), e.g. when using Matheison chlorine dioxide production method. This causes sodium losses that need to be compensated for also with more make-up chemicals.</p> <p>Although ClO₂ is an excellent de-lignifying and bleaching agent that selectively oxidises lignin and extractives, it is also difficult to handle in full-scale applications due to toxicity and its high reactivity in the gaseous form.</p> <p>Effluent tail gas chlorine from chlorine dioxide stripping systems is often converted to hypochlorite by hydroxide scrubbing.</p> <p>Up to 0.8 tonnes of chlorine per tonne of chlorine dioxide can be present depending upon the chemical production route selected to produce the chlorine dioxide. [EIPPCB BREF, 2001]</p>
<p>19. Reinforced Alkaline Extraction</p> <p>Alkaline extraction bleaching stage using</p>	<p>For example (EO) and (EOP) stages.</p> <p>Applied before a final chlorine dioxide stage.</p>	<p>Widely used technique.</p> <p>(EO) has modest additional investment costs.</p> <p>Investment costs of 1500 ADt/d ECF bleaching system are 8-10</p>	<p>Advances in mixer technology mean oxygen can be mixed ahead of extraction.</p> <p>Can shorten bleaching sequences.</p>

Management Options	Release Characteristics	Applicability	Other Considerations
sodium hydroxide with subsequent addition of oxygen and hydrogen peroxide solution as a rein-forcing agent.	Enhances oxidising bleaching effect and lignin removal in the extraction stage.	MEuros at new mills and 3-5 MEuros at existing mills. The operating costs are 10-12 MEuro/a. 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. [EIPPCB BREF, 2001]	Transition metals need to be controlled when using peroxide.
20. Acid Chelation for ECF and TCF Acidic stage where chelating agent EDTA or DTPA used for removal of metals.	In conventional bleaching sequences, the decomposition of peroxide can be controlled by removing transition metals by prior acid washing and/or a chelation Q stage. Transition metal control is important prior to peroxide Bleaching. Transition metal control needed to reduce bleaching chemical consumption / losses through catalysed degradation.	ECF and TCF bleaching using peroxides (also ozone to some extent).	Chelation agents discharged to the aquatic environment risk remobilisation of heavy metals in sludges. [EIPPCB BREF, 2001] Neutral pH chelation to retain magnesium ions may be performed.
21. Increased Closure of the Bleach Plant Reduce chlorides in the system. Attempt to use counter current wash water flows.	TCF or ECF mills using modest amounts of chlorine dioxide will be able too increase the degree of closure of the bleach plant. With reduced bleachery wastewater quantities, effluent treatment becomes easier. Peroxide, chlorine dioxide and alkaline extraction stages benefit from increased system temperatures caused by closure. Reduced energy consumption.	Kraft mills and sulphite mills (magnesium and sodium based) with recovery. General ECF and TCF applicability. ECF and TCF partial closure possible. Full closure not yet achieved due to accumulation of dissolved substances – corrosion issues. Possible to utilise ECF and TCF alkaline waters to wash unbleached pulp entering bleachery.	Increased temperature effects caused by closure may affect pulp strengths. Wood based general aquatic toxicity is reduced. TCF offers the potential to further close up mill systems in the future to reduce effluent to water (including non UPOP AOX and non-chlorinated toxic compounds in general) by counter current bleach stage liquids being led through the oxygen stage and then through brown stock washing to the recovery system.
22. De bottlenecking Recovery Boiler Forward planning.	Forward planning of process to build in capacities to cope with advances in: Extended Cooking; Modified Cooking; Oxygen de-lignification; Spills collection and recovery of TCF effluents. See Extended Cooking; Modified Cooking and Oxygen de-lignification above.	Generally, the impact of extended cooking and also oxygen de-lignification on production is very site specific.	If the chemical recovery system is a bottleneck at a mill then introduction of extended de-lignification risks a loss in production due to the increased demand on that part of the system.
23. De bottlenecking Chlorine Dioxide Manufacture Forward planning.	Forward planning of process to build in capacities to cope with advances in bleaching. See chlorine dioxide protection, and substitution above.	Increased substitution and ECF bleaching.	Recovery cycle implications also. The intake of sulphur to the inorganic chemical balance when operating with a high proportion of chlorine dioxide in bleaching means a high amount of sulphur may have to be discharged or disposed as neutral salts (e.g. Na ₂ SO ₄). E.g. when using Matheison chlorine dioxide production method. This causes sodium losses that need to be compensated for also with more make-up chemicals.

Management Options	Release Characteristics	Applicability	Other Considerations
<p>24. TCF Methods</p> <p>Prolonged selective de-lignification down to low kappa numbers allows oxygen bleaching chemicals to be used.</p> <p>Totally Chlorine Free (TCF) bleaching is a bleaching process carried out without any chlorine containing chemicals. In TCF bleaching hydrogen peroxide together with ozone or peracids are the most commonly used chemicals.</p> <p>It may be possible for TCF bleaching effluents to go to the recovery cycle.</p>	<p>In TCF bleaching the formation of dioxins and furans is zero.</p> <p>The easiest way to bleach without chlorine chemicals is to use several peroxide stages.</p> <p>Peroxide stages may be relatively easily applied to a bleachery designed for conventional bleaching.</p> <p>An O-Q(PO) sequence for non woods does not need the high cost corrosion protection needed when using chlorine dioxide and some of the existing equipment in a CEH sequence can be used when converting to O-Q(PO).</p> <p>Ozone may be used to activate the fibres towards peroxide.</p>	<p>A general drawback of TCF bleaching compared with chlorine and ECF bleaching is that a low kappa number is needed prior to bleaching. This is possible only by using methods (extended cooking, oxygen de-lignification) that result in a lower final yield.</p> <p>Kraft - TCF-bleaching: The investment costs for a 1500 Adt/d TCF bleaching plant are 7-8 MEuros at new mills and 2-5 MEuros at existing mills depending on the materials of the existing bleaching equipment. Operating costs are higher (18-21 MEuro/a) than in ECF-bleaching due to higher chemical costs. [EIPPCB BREF, 2001]</p> <p>Sulphite: N.B Chlorine dioxide bleaching is no longer used in Europe, with most sulphite mills producing TCF pulps. Mostly oxygen, sodium hydroxide and hydrogen peroxide. TCF bleaching sulphite plant 700 Adt/day conversion costs 20 – 30 MEuros. However TCF conversion can save on operating costs (chemicals and energy). [EIPPCB BREF, 2001]</p> <p>Sulphite: N.B. Chlorine dioxide is still used in North America.</p>	<p>Any replacement of chlorine chemicals in bleaching further reduces the production of AOX. Although a combination of oxygen de-lignification or extended cooking and full chlorine dioxide substitution in bleaching produces only minute quantities of AOX in effluents, these low AOX quantities can be reduced even further by using TCF.</p> <p>In 1998 6% of the world market was TCF pulp.</p> <p>Transition metal control is important and so EDTA and DTPA releases to water an issue (See Acid Chelation).</p> <p>TCF pulps have lower strength properties than chlorine and ECF bleached pulps. This can be compensated for by lower brightness if this is acceptable. TCF product quality does not meet all users' required pulp properties.</p> <p>TCF offers the potential to further close up mill systems in the future to reduce effluent to water (including non UPOP AOX and non-chlorinated toxic compounds in general) by counter current bleach stage liquids being led through the oxygen stage and then through brown stock washing to the recovery system.</p>
<p>25. Hydrogen Peroxide – P Stage</p> <p>Especially for bleaching wood or non-wood sulphite fibres.</p>	<p>In TCF bleaching the formation of dioxins and furans is zero</p> <p>Not a very efficient de-lignifier.</p> <p>Easily applied to existing bleachery equipment layouts.</p> <p>Kappa may be higher than that achieved after chlorine chemical bleaching.</p>	<p>ECF and TCF bleaching.</p> <p>Sulphite pulp bleaching.</p> <p>A pressurised PO stage can be added to the end of an existing mill bleach plant to enable ECF pulps to be produced without having to increase chlorine dioxide capacity.</p> <p>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. [EIPPCB BREF, 2001]</p>	<p>There is also enhanced efficiency pressurised / reinforced peroxide (PO). However this requires pressurised equipment and so only a good solution for new installations.</p> <p>Difficult to attain very high brightness with kraft pulps.</p> <p>Transition metal control is important prior to peroxide Bleaching. Transition metal control needed to reduce bleaching chemical consumption / losses through catalysed degradation. See 18. Acid chelation above.</p>
<p>26. Ozonation – Z Stage</p>	<p>In TCF bleaching the formation of dioxins and furans is zero</p> <p>More selective bleach than hydrogen peroxide.</p>	<p>ECF and TCF bleaching.</p> <p>Expensive, specialist equipment and process control, ozone generation equipment needed, energy costs high.</p>	<p>If kappa is high then chlorine dioxide can be used synergistically with ozone as (DZ) or (ZD) treatments in ECF bleaching.</p> <p>High final TCF brightness possible. Can give</p>

Management Options	Release Characteristics	Applicability	Other Considerations
	Also activates fibres towards peroxide. Not applicable to conventional bleachery equipment.	TCF oxygen chemicals make closure of washing filtrate systems possible. Ozone used with ECF plant can give pulp with same papermaking properties. 1500 ADT/d mill 12-15 MEuros. 1.8 – 2.1 Meuros/a operating costs. [EIPPCB BREF, 2001]	completely chlorine-free bleaching for any brightness. N.B. Ozone readily attacks cellulose.
27. TCF Sequences Conversion of older chlorine bleacherie s utilising existing plant layouts.	In TCF bleaching the formation of dioxins and furans is zero. (O)QWQPP (O)QPP (O)QWPPP	Existing plant. The existing layout of a bleachery determines the viability and cost of conversion.	
28. TCF Sequences New plant bleacherie s - peroxide	In TCF bleaching the formation of dioxins and furans is zero. (O)Q(PO) (for non woods) (O)QP (O)QPPP (O)Q(EOP)Q(PO)	New plant. New plant bleacherie s have the advantage of not needing to utilise existing equipment.	
29. TCF Sequences New plant bleacherie s – peroxide and ozone	In TCF bleaching the formation of dioxins and furans is zero (O)QPZP is used widely for softwoods. (O)(ZQ)PZP (O)(ZQ)P(ZQ)P	New plant. New plant bleacherie s have the advantage of not needing to utilise existing equipment.	
30. TCF Sequences New plant bleacherie s – ozone and peroxide reinforced	In TCF bleaching the formation of dioxins and furans is zero (O)Q(PO)Z(PO) (O)(ZQ)(PO)	New plant. New plant bleacherie s have the advantage of not needing to utilise existing equipment	
Secondary Measures - Effluent Treatments			
31. Effluent Treatments Kraft and Sulphite - Use adequately performing primary and secondary biological treatments.	Secondary treatment removes biodegradable materials via degradation and also non biodegradables via adherence to sludge biomass. Dioxins, furans and DDT will be removed almost totally. Other pesticide POP's less so. [EA S6.01, 2000]	Aerobic oxygen systems can be retrofitted to existing plant. The use of air minimises energy consumption. The investment costs amount to 2.6 MEuros for a kraft pulp mill with a capacity of 250000t/a and 3.8 MEuros for a mill with 500000 t/a capacity respectively. The investment costs for	Aerobic - Higher aerobic operating temperatures aid degradation. Climatic conditions important. Aerobic - Large settlement lagoons have other benefits allowing high capacity for post treatment storage in case of problems (See Spills)

Management Options	Release Characteristics	Applicability	Other Considerations
	<p>A well designed and operated secondary treatment plant is capable of removing up to 90% of TCDD and TCDF in effluents. [USC, 1989]</p> <p>Aerobic - oxidation ponds, air or oxygen aeration or activated sludge operating at <0.15 kg BOD/kg MLSS*day.</p> <p>Anaerobic – Higher load lower flow (high strength) process effluents need anaerobic treatment. More effective in ring compound degradation and chlorate removal (see chlorine dioxide manufacture). Aerobic systems should be followed by an aerobic one.</p> <p>Total AOX % reduction at EU Kraft mills sedimentation and biological treatment for Aerated lagoons (20%-45%) and Activated sludge (40%-65%). . [EIPPCB BREF, 2001]</p> <p>Large settlement lagoons needed for final solids removal / effluent clarification.</p> <p>Emission levels for non-integrated and integrated bleached Kraft and sulphite pulp mills per tonne of pulp. = AOX 0.25 kg/Adt after biological treatment. . [EIPPCB BREF, 2001]</p>	<p>chemical precipitation includes equalisation tank, chemical dissolving equipment, chemical dosing equipment, precipitation and flocculation unit and tertiary clarifier. Operating costs amount to about 50000 Euros being somewhat lower for the mill with less capacity. [EIPPCB BREF, 2001]</p>	<p>Oxidation ponds work best in warm climates. Inexpensive, low maintenance and act as emergency impoundments. Large areas are required for these shallow ponds. Aerated ditches can be used also. Aeration and nutrient addition reduce retention times.</p> <p>Activated sludge – low retention times, twice as expensive as aerated ponds.</p> <p>Anaerobic - High process water temperatures advantageous. (See Closure).</p> <p>Secondary treatment reduces overall toxicity of effluents.</p> <p>Primary treatment including solids settlement, neutralisation, cooling and equalisation will protect the secondary treatment system from shocks and excessive loads (spills for example). In this respect the installation of upstream process buffer storage capacity for hot or concentrated streams is also applicable for both existing and new mills as a basic general protection measure for the effluent treatment system. (See Spills).</p>
<p>32. Spill Control</p> <p>Install accommodation for holding upstream process liquors or concentrated waters in case of emergency.</p>	<p>Protect the effluent treatment system from shocks and excessive loads from spills and stream handling problems.</p>	<p>Large settlement lagoons have other benefits allowing high capacity for post treatment storage in case of problems.</p> <p>Upstream buffer tanks: Investment costs for 1500 Adt/day production about 0.8 - 1.0 MEuros for two 3000 m³ buffer storage tanks including necessary piping, insulation and pumps with electrification and process control. . [EIPPCB BREF, 2001]</p>	<p>Oxidation ponds act as temporary impoundments in emergencies. Large area required for these shallow ponds. Aerated ditches can be used also.</p> <p>Effluent treatment equalisation basins will also protect secondary treatment systems from shocks and excessive loads (spills for example). In this respect the installation of upstream process liquor or water buffer storage capacity for hot or concentrated streams is also applicable for both existing and new mills as a basic general protection measure for the effluent treatment system.</p>
<p>Secondary Measures – Recovery Combustion</p>			
<p>33. De-inking Sludge Disposal</p> <p>De-inking sludge UPOPs concentrations need to be known. Quantify and report.</p>	<p>De-inking sludge UPOPs concentration (needs to be known). Quantify and report.</p> <p>Refer to the incineration guidance.</p> <p>Controls needed if disposal route is via waste</p>	<p>RCF de-inking mills.</p>	

Management Options	Release Characteristics	Applicability	Other Considerations
Incinerate sludge in appropriately designed and operated plant with energy recovery.	application to land for agricultural benefit.		
34. Recovery Boiler Combustion of black liquor.	Attention has to be paid in all cases to good combustion conditions in order to minimise the formation of UPOPs. Combustion plant design, residence times and temps, abatement etc. Even under the most unfavourable conditions a temperature of > 850 °C has to be maintained for at least two seconds to destroy PCDDs/PCDFs and to avoid precursors (if more than 1 % of halogenated organic substances, expressed as chlorine, are incinerated, the temperature has to be raised to at least 1100 °C).	Larger mills.	Refer to the combustion guidance. Oxygen and CO in the combustion chamber and retention time of the flue gas in the cooling system heavily influence the dioxin and furan in the flue gases. Good combustion conditions and short retention times of the flue gases in the waste heat recovery boiler and a very fast lowering of the flue gas temperature below 250°C are additional measures to minimise dioxin and furan emissions. Continuous feed of homogeneous fuel and the reduction of the availability of halogens in the combustion chamber by the exclusion of fuels with a high halogen content.
35. Process Sludge Combustion Incineration of RCF De-inking, bleachery and treatment sludges. in suitably designed boilers with energy recovery. Monitoring of sludge feed contamination levels.	RCF fibre supply may have high UPOPs contamination levels, PCBs etc Chlorinated bleaching derived compounds will be contained in treatment sludges. Attention has to be paid in all cases to good combustion conditions in order to minimise the formation of UPOPs. Combustion plant design, residence times and temps, abatement etc. See below. Fluidised bed combustors are flexible and robust in handling variable feedstocks.	Larger mills. RCF de-inking mills.	Refer to the combustion guidance. Oxygen and CO in the combustion chamber and retention time of the flue gas in the cooling system heavily influence the dioxin and furan in the flue gases. Good combustion conditions and short retention times of the flue gases in the waste heat recovery boiler and a very fast lowering of the flue gas temperature below 250°C are additional measures to minimise dioxin and furan emissions. Continuous feed of homogeneous fuel and the reduction of the availability of halogens in the combustion chamber by the exclusion of fuels with a high halogen content.
36. Auxiliary Boilers Combustion of bark, incineration of sludges, RCF contraries and plastics	Attention has to be paid in all cases to good combustion conditions in order to minimise the formation of UPOPs. Combustion plant design, residence times and temps, abatement etc. Even under the most unfavourable conditions a temperature of > 850 °C has to be maintained for at least two seconds to destroy PCDDs/PCDFs and to avoid precursors (if more than 1 % of halogenated organic substances, expressed as chlorine, are incinerated, the temperature has to be raised to at least 1100 °C).	Larger mills. RCF de-inking mills	Bark salt issue, RCF chlorinated plastic wastes PVC etc. Refer to the combustion guidance. Oxygen and CO in the combustion chamber and retention time of the flue gas in the cooling system heavily influence the dioxin and furan in the flue gases. Good combustion conditions and short retention times of the flue gases in the waste heat recovery boiler and a very fast lowering of the flue gas temperature below 250°C are additional measures to minimise dioxin and furan emissions. Continuous feed of homogeneous fuel and the reduction of the availability of halogens in the combustion chamber by the exclusion of fuels with a high halogen content.
Secondary Measures –			

Management Options	Release Characteristics	Applicability	Other Considerations
<p>Others</p> <p>37. Materials Transport and Storage</p> <p>An issue in some regions.</p> <p>Dioxins and furans emitted from coastal pulp and paper mills have been created through the burning of salt contaminated hogged fuel.</p> <p>Wood – coastal log transport.</p> <p>Bamboo - is sometimes floated to the mill in large bamboo rafts.</p>	<p>Transport and storage modes - fibre uptake of sea salt (hogging).</p> <p>Logs transported and stored in salt water take up chlorine into the bark. The bark is stripped from the logs and ground up to produce “hogged” fuel. This material is then used as boiler fuel to produce heat and electrical energy for the pulp and paper process.</p> <p>Given the natural source of fibre - wood grass etc - it is not technically possible to totally starve, of chlorine, any combustion process using such feedstock. Thus whilst there are measures to reduce excess or unavoidable chlorine in combustion feedstock, attention has to be paid in all cases to good combustion conditions in order to minimise the formation of UPOPs.</p> <p>There may be other fibre sources with potential for salt uptake in estuarine / littoral environments.</p>	<p>Coastal and estuarine mills employing water transport methods.</p>	<p>This was a particular issue in British Columbia, Canada. A Canadian strategy was to be produced by 2001 - Chemical and mechanical Pulping Canadian strategy (BC) on coastal log transport to include: maximum allowable salt content for hogged fuel, removal of chloride from logs, hogged fuel washing and pressing, options for blending hogged fuel of different salt levels, alternatives to log handling, transportation and storage practices that rely on salt water, impacts of the length of time entailed in transportation and storage on the salt content of hogged fuel, inclusion of transportation modes and effects in eco-certification criteria, in-plant opportunities to avoid creation of dioxins and furans, alternative fuel opportunities and costs.</p>
<p>38. Fibre Selection and Storage</p> <p>Timber, wood chips, hemp etc. should not have been sprayed with harmful substances, e.g. lindane or pentachlorophenol (PCP).</p> <p>Drainage from storage areas via treatment system</p>	<p>Pesticide run off from storage and processing areas.</p> <p>Polychlorinated phenols, which can contain dioxins and furans and precursors, are used as fungicides to preserve and protect wood. When a mill uses chips from wood treated in this way, dioxins and furans could be released both in the final products and in the waste water from the mills unless TCF bleaching used. [CBNS, 1996]</p> <p>N.B Use of PCP in stored / shipped cotton.</p>	<p>Some UPOPs pesticides still in use in some parts of the world.</p>	<p>N.B Canada has a CEPA regulation that prohibits the use of wood chips that origin from wood preservation activities (treated with polychlorinated phenol substances)</p>
<p>39. Effluent Treatment Sludge Management:</p> <p>De watering and incineration in suitably designed boilers with energy recovery.</p>	<p>Attention has to be paid in all cases to good combustion conditions in order to minimise the formation of UPOPs.</p> <p>Alternatively it could be applied to land where ECF used (subject to analysis).</p>	<p>Larger mills.</p> <p>All effluent treatment sludges.</p>	<p>Non biodegradable UPOPs are be taken out of the effluent stream and into the sludge via adherence to sludge biomass.</p>
<p>40. Combustion Flue Dust Management:</p> <p>Control of dust utilisation, management or disposal.</p> <p>Concentrations need to be known to inform disposal choices.</p>	<p>Concentration of dioxin and furan occurs in abatement dusts.</p> <p>These need to be managed in the same way as other special wastes.</p> <p>Should not be combined with bottom ash.</p> <p>Flue dust should not be spread on land.</p>	<p>Mills with recovery and other abated combustion processes.</p>	<p>Licensing and waste regulation?</p> <p>Flue dust concentrates abated species and is distinct from bottom ash.</p>

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Appendix 2

Existing Supra-national, National and Sub-national Guidance**1 European Union - EU IPPC Pulp and Paper BREF**

Standards are contained in the BREF [EIPPCB BREF, 2001]

The following emission levels are associated with the use of a suitable combination of best available techniques achieved after primary and biological treatment (and to air):

Parameter	Units	Bleached Kraft ¹ after Primary Treatment	Bleached Kraft ¹ after Biological Treatment	Integrated Unbleached Kraft ² after Primary Treatment	Integrated Unbleached Kraft + kraftliner, sackpaper	Integrated Bleached sulphite ¹	To air
AOX	kg/ADt	(-) - 0.4	(-) - 0.25	(-)*	(-)	(-)* TCF	-
Wastewater	M ³ /ADt	30 - 50		15 - 25	15-25	40 - 55	-
PCDD/PCDF**	ng/m ³ ITEQ	-	-	-	-	-	0.1

Notes:

*This parameter is not relevant here. Low emissions of AOX may occur from re-pulping of purchased bleached pulp.

1) Emission levels for non-integrated and integrated bleached Kraft and sulphite pulp mills per tonne of pulp.

2) Unbleached Kraft pulp mills are all integrated mills. They produce kraftliner, unbleached board grades and sack and other Kraft paper. Many of them use recycled fibres and purchased bleached pulp. Higher emission levels are usually found in mills using more recycled fibres as raw material. Figures are per tonne of liner/paper/board produced

**Information about PCDD/PCDF emissions to air and water has not been reported in the Pulp and Paper BREF. Information about PCDD/PCDF emissions to air is given in other BREFs; 0.1 ng/m³ I-TEQ can be seen as standard.

Dioxin - Measurement is via EN 1948, the official reference method for Dioxins in the EU and EFTA states. Long-term or on-line measurement systems must give equivalent results if these devices are to be installed for monitoring purposes. A 6-monthly sampling period (3-monthly in first 12 months of operation), average value over sample period of ½ - 8 hours).

AOX - Measurement in Scandinavia AOX is analysed according to SCAN-W 9:89, the corresponding German AOX method, DIN 38409, H14, is basically very similar to the Scandinavian method. The ISO standard (ISO 9562:1998) has been available since 1998 and there is also the European Norm, EN 1485 - Determination of adsorbable organically bound halogens, available. There are minor differences between these measurement methods but they do not give significant variations in analytical values.

2. Canada

Canada has two regulations that apply to effluents:

A - Pulp and Paper Mill Defoamer and Wood Chip Regulations (SOR/92-268).

The purpose of these Regulations is to prevent the formation of dioxins and furans and limit the discharge of these substances from pulp and paper mills using a chlorine bleaching process. The defoamers used by pulp and paper mills are limited to a maximum concentration of ten parts per billion of dibenzodioxin (DBD) and forty parts per billion dibenzofuran (DBF). In addition, The Regulations stipulate that "no person shall import, offer for sale, sell for use or use in a mill in Canada, wood chips that have been made from wood that has been treated with polychlorinated phenols". See http://www.ec.gc.ca/NOPP/DIVISION/EN/detail.cfm?par_docID=99

B - Pulp and Paper Mill Effluent Chlorinated Dioxins and Furans Regulations (SOR/92-267).

The Regulations are designed to protect the environment and humans from dioxin and furan releases. The Regulations prohibit the releases of dioxins and furans in pulp and paper mill

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effluents as of July 1, 1992. In the case of many of the existing mills, significant modifications to the bleaching processes were necessary to avoid dioxin and furan formation. The Regulations require mill operators to collect composite samples of their final effluent and report on concentrations of dioxins and furans. the frequency of sampling is set as quarterly between July 1, 1992, and December 31, 1993, and monthly commencing January 1, 1994. In 1995, a mill may adopt quarterly sampling if it has had no measurable concentrations in its last three consecutive monthly samples. A mill may adopt annual sampling if it has had no measurable concentrations in its last three consecutive quarterly samples. The Regulations require that a mill revert back to monthly testing if either a quarterly test or an annual test detects dioxins or furans. This graduated testing schedule was adopted because testing is complex and costly compared with testing for conventional pollutants. See http://www.ec.gc.ca/NOPP/DIVISION/EN/detail.cfm?par_docID=86

Emissions to air from bark boilers (coastal mills) have numeric targets and a timeframe for achieving target dioxin and furan emissions of less than 0.1 ng/m³ TEQ for new boilers and less than 0.5 ng/m³ TEQ for all existing boilers by 2006. Tested twice per year initially and then annually after 2003. Testing and reporting will be performed using methods and procedures acceptable to the responsible provincial ministry

Canadian limits are therefore:

Parameter	Media	Units	Limit	Sampling	Comments
PCDD / PCDF	To air	ng/m ³	New 0.1 Existing 0.5	6 monthly then Annually	Coastal mills. Hogged fuel.
PCDD / PCDF precursors DBD and DBF	In defoamer process chemicals	Ppb Ppb	DBD 10 DBF 40	-	-
PCDD / PCDF	To water		No measurable concentration of 2,3,7,8-TCDD or 2,3,7,8-TCDF.	Monthly or Quarterly or Annually	Graduated sampling due to complexity and cost

Dioxin – Measurement is via the Reference Method for the Determination of Polychlorinated Dibenzopara-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) in Pulp and Paper Mill Effluents, published by the Department of the Environment, Report EPS 1/RM/19, 1992, as amended from time to time; (méthode de référence).

AOX limits are not set in Canadian Federal Laws.

British Columbia Regulation B.C. Reg. 470/90 (including amendments up to B.C. Reg. 188/2002) specifies the tightest limit of 0.6 kg/Adt AOX for bleached kraft sulphate mills and 1.0 kg/Adt AOX for bleached sulphite mills. Other Canadian Provinces have their own AOX limits also.

3 USA – EPA Cluster Rules

The USA's Clean Water Act (CWA, Federal Water Pollution Control Act, FWPCA) provides a national framework for issuing point source discharge permits. It is administered by the EPA and states (which may add their own regulations). The EPA's Cluster Rule [USEPA, 2003] updates and amplifies the Clean Water Act. Some of the main aspects are given below, but the actual Rule contains more detail and can be accessed on the EPA Web site: www.epa.gov/OST/pulppaper/.

At bleached kraft (and soda) mills (Subpart B) the limits for existing sources (pretreatment standards for existing sources, PSES) and new sources (new source performance standards, NSPS) for continuous dischargers are:

Parameter	Existing Source	Existing Source	New Source	New Source
	Daily Maximum	Monthly Average	Daily Maximum	Monthly Average
AOX (kg/metric ton)	0.951	0.623***	0.476	0.272***
2,3,7,8-TCDD (ng/m ³)*	not applicable	< ML**	not applicable	< ML**
2,3,7,8-TCDF (ng/m ³)*	not applicable	31.9	not applicable	31.9

Notes:

* Refer to bleach plant effluent.

** < ML means less than the minimum level at which the analytical system gives recognizable signals and acceptable calibration point.

*** New plant limit of 0.208 kg/metric tonne and existing plant limit of 0.512 kg/ metric tonne yearly average for non continuous discharges (final effluent).

Dioxin – Measurement is via Method 1613, for TCDD and TCDF, promulgated on September 15, 1997 (62 FR 48394).

AOX – Measurement is via Method 1650 for each leaching kraft line specified in Cluster Rules.

Best Available Technology (BAT) is required for bleaching. Namely, ECF approaches: For existing sources, Option A, which includes: chip thickness control; closed brown stock screening, so that filtrates go to chemical recovery; dioxin-free antifoams; brown stock washing to 10 kg Na₂SO₄/ad metric ton of pulp (equivalent to 99% pulping chemicals recovery from pulp); E-stage reinforcement (eg: EO or EP) to eliminate any H-stage and/or allow lower kappa factor in first stage; strategies to minimize dioxin precursors in brown stock and to minimize kappa factor; high shear mixing of chemicals; biological treatment of effluent to remove 90% of BOD₅. For new sources, Option B, which is Option A plus extended prebleaching lignin removal in the form of extended delignification and/or oxygen delignification. For Sulphite mills “Sufite mills (Subpart E)”, the Best Available Technology (BAT) for bleaching includes TCF (but not necessarily oxygen delignification), but ECF for ammonium based mills - for both existing and new sources.

4 World Bank Guidance

The World Bank Pollution Prevention and Abatement Handbook 1998 - Toward Cleaner Production (Pulp and Paper Mills Page 397) [World Bank, 1998] details the following:

Target Pollution Loads and techniques (before abatement) for New Installations:

Step	Units	Limit	Target	Technology
Mill Wastewater Generation	m ³ /t ADP	<50	20	
Paper Mill Effluent discharges	m ³ /t ADP	<5		
Bleaching				Total closure TCF where feasible, incinerate bleachery effluents in recovery boiler
Sludges				Dewatering treatment sludges and incineration in bark boiler or fossil fueled boilers.

Emission Guidelines – Liquid Effluents from New Pulp and Paper Manufacturing

Parameter	Units	Target	Maximum Value	Comments
AOX Retrofits	mg/l and kg/t	8 / 0.4	40 / 2	Cl ₂ not to be used
AOX New Mills	mg/l and kg/t	4 / 0.2	40 / 2	Cl ₂ not to be used
AOX Papermill	mg/l		4	Cl ₂ not to be used

5 The United Kingdom

The UK's Integrated Pollution Prevention and Control (IPPC) Technical Guidance for the Pulp and Paper Sector [EA S6.01, 2000] details the following:

Relevant Benchmark Emission Values

Media	Substance	Activity	Benchmark value	Basis for the Benchmark
To air	Chlorine		5 mg/m ³	
To air	Chlorine dioxide	Bleaching/ broke recovery	1 mg/ m ³	Parity with UK chemical sector (Note1)
To water	AOX	All paper (Tissue) mills	10 g/ADt	Paper mills using wet strength agents (Note 2)
To water	AOX	All pulping mills	-	AOX limits not set (Note 2)
To air	Dioxins	Liquor burning	1 ng/m ³	Parity with other UK industrial sector benchmarks
To air	Dioxins	Other combustion, co-combustion	0.1 ng/m ³ ITEQ	(Note 3)

	and incineration		
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Notes:

1. Chlorine bleaching should have been phased out.
2. AOX (absorbable organic halogen) is a measure, used widely in this industry, which includes the more harmful, highly substituted chlorinated organics, such as PCP, as well as those with lesser substitution as long as they are absorbable. It was the main measure in the drive away from chlorine bleaching. Below a level of around 1.5 kg/ADt the correlation of AOX level with toxicity or harm becomes harder to demonstrate. There are no mills in the UK which release AOX at such levels. Most mills in the UK release less than 5 g/ADt, although some sectors, such as tissue making, use chlorine based wet strength agents which will increase AOX although with lower substituted compounds. Tissue mills should not exceed 10 g/ADt. It is not normally necessary to set AOX limits in permits.
3. EU Waste Incineration Directive 2000/76/EC, UK Incinerator Sector Guidance Note IPPC S5.01, 2003 consultation document; IPC S2 1.01 Combustion processes: large boilers and furnaces 50MW(th) and over November 1995, £9.95 ISBN 0-11-753206-1; IPC S3 1.01 Combustion Processes supplements IPR 1/2, IPC S2 1.01, S2 1.03 to S2 1.05; Part B PG1/3 Boilers and Furnaces 20-50 MW net thermal Input (ISBN 0-11-753146-4-7); Part B PG1/4 Gas Turbines 20-50 MW net thermal Input (ISBN 0-11-753147-2) and Incinerator Sector Guidance Note IPPC S5.01 Consultation Document, Issue 1 August, 2003.

Dioxins – Measurement is via Method EN 1948 Parts 1,2 and 3 - 1996 - Determination of the mass concentration of PCDDs/PCDFs is used. Extractive sample train GC/MS 4 hour minimum 8 hour maximum 0.1 ng I-TEQ/m³ calculated.

AOX – Measurement is via Method ISO 9562: 1998, and EN 1485 - Determination of adsorbable organically bound halogens.

Conditions in Permits can be set with percentile, mean or median values over annual, monthly or daily periods, which reflect probable variation in performance. In addition, absolute maxima can be set. Where there are known failure modes, which will occur even when applying BAT, limits in Permits may be specifically disapplied, but with commensurate requirements to notify the Regulator and to take specific remedial action.

For water: UK benchmarks or limits are most frequently 95 percentile concentrations or absolute concentrations, (with flow limited on a daily average or maximum basis).

For air: Benchmarks or limits are most frequently expressed as daily averages or, typically 95 percent of hourly averages.