GUIDELINES ON BEST AVAILABLE TECHNIQUES AND PROVISIONAL GUIDANCE ON BEST ENVIRONMENTAL PRACTICES

relevant to Article 5 and Annex C of the Stockholm Convention on Persistent Organic Pollutants

Production of pulp using elemental chlorine or chemicals generating elemental chlorine

UNEP

Stockholm Convention

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May 2007, Geneva, Switzerland

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V.C Production of pulp using elemental chlorine or chemicals generating elemental chlorine

Summary

The main processes involved in making pulp and paper products are raw material handling and preparation, storage (and preservation for non-woods), wood debarking, chipping and agricultural residue cleaning, deknotting, pulping, pulp processing and bleaching if required and, finally, paper or paperboard manufacturing.

Of the chemicals listed in Annex C of the Stockholm Convention, only PCDD and PCDF have been identified as being produced during the production of pulp using elemental chlorine. Of the 17 PCDD/PCDF congeners with chlorine in the 2,3,7 and 8 positions, only two congeners – namely 2,3,7,8-TCDD and 2,3,7,8-TCDF – have been identified as potentially being produced during chemical pulp bleaching using chlorine. Most of the formation of the 2,3,7,8-TCDD and 2,3,7,8-TCDF is generated in the C-stage of bleaching via the reaction of chlorine with precursors of TCDD and TCDF. HCB and PCB are not formed during pulp bleaching.

As a summary, the following primary measures can be taken for decreasing or eliminating the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF in wood and non-wood bleaching processes: eliminate elemental chlorine by replacing it with chlorine dioxide (elemental chlorine-free bleaching) or in some cases with totally chlorine-free processes; reduce application of elemental chlorine by decreasing chlorine multiple or increasing the substitution of chlorine dioxide for molecular chlorine; minimize precursors such as dibenzo-*p*-dioxin and dibenzofuran entering the bleach plant by using precursor-free additives and thorough washing; maximize knot removal; and eliminate pulping of furnish contaminated with polychlorinated phenols.

1. Introduction

The following draft guidelines provide guidance on best available techniques and best environmental practices for chemical pulp bleaching using elemental chlorine or chemicals generating elemental chlorine. Within a pulp bleaching plant, PCDD/PCDF may be released at several stages in the process: in the effluent discharged to water or land; from emissions to air from the recovery boilers (reference to section VI.E.); and residues sent to landfill (reference to section III.C. (ii) of the present guidelines).

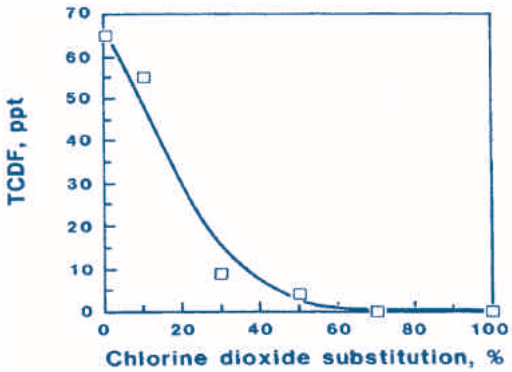
The chemicals listed in Annex C of the Stockholm Convention include polychlorinated dibenzo-*p*-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), hexachlorobenzene (HCB) and polychlorinated biphenyls (PCB). Of these, neither HCB nor PCB is or has been unintentionally produced during chemical pulp bleaching. Furthermore, of the 17 PCDD/PCDF congeners with chlorine in the 2,3,7 and 8 positions and which are considered to express dioxin-like toxicity, only two, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF), have been identified as potentially being produced during chemical pulp bleaching. Therefore any

best available techniques and best environmental practices in the context of chemical pulp bleaching using elemental chlorine or chemicals generating elemental chlorine should be directed at reduction and elimination of 2,3,7,8-TCDD and 2,3,7,8-TCDF. The adsorbable organic halogen (AOX) compounds do not correlate with dioxins or furans and are therefore not discussed here.

In the mid-1980s the discovery of dioxins and furans in effluents from pulp mills using chlorine and hypochlorite in their bleaching sequences prompted extensive research into how to reduce or eliminate their formation. The intense international research showed that the principle mechanism for formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF is the chlorination of the precursor compounds dibenzodioxin (DBD) and dibenzofuran (DBF) present in the unbleached pulp via aromatic electrophilic substitution. The formation of 2,3,7,8-TCDF will be reduced by increasing chlorine dioxide substitution, as shown in Figure 1. The use of molecular chlorine in bleaching has been largely replaced by chlorine dioxide (ECF, elemental chlorine-free) and other oxygen-based chemicals such as molecular oxide, peroxide and ozone (TCF, totally chorine-free).

Over 80% of all chemical pulp comes from the kraft process (Gullichsen and Fogelholm 2000). However, over 10% of world pulp production is made from non-wood fibres and in some countries, for example China and India, it is the dominant fibre source. In China, over 24 % of the pulp used in the paper industry is produced from wheat straws, reed, bamboo other and non-wood sources, whereas in Western countries the use of non-wood sources is currently very small. The average plant processing non-wood raw material is about one fifth of that in world. In 1998, 107 Nordic paper and board mills produced 25 million tons of products, while about 6,000 Chinese mills produced 28 million tons (Edelmann et al. 2000). In 2005 about 3600 Chinese mills produced 56 million tons of paper and board (2005 annual report of China paper industry).

Figure 1. Elimination of 2,3,7,8-TCDF with increasing substitution of chlorine dioxide for chlorine



1.1 Raw materials

Pulp and paper are manufactured from wood-based materials and from many kinds of non-wood materials, such as straw, bagasse, bamboo, reeds and kenaf. At present, wood provides over 90% of the world's virgin fibre requirement while non-wood sources provide the remainder. In 2005, the production of wood-based chemical pulps was about 126 million tons and the production of non-woods 17 million tons (statistics from *FAOSTAT*). Non-wood pulps are mainly produced in developing countries, but for many reasons non-wood pulp fibres are gaining new interest in Eastern and Western Europe as well as in North America (Paavilainen 1998).

Wood and the main non-wood materials used in papermaking represent a complex mixture of the same substances – cellulose (40–45%), hemicelluloses (25–35%), lignin (20–30%) and extractives (2–15%). 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, dissimilar. They differ considerably in their morphological and chemical characteristics, which make them suitable for varying grades of final products (Paavilainen 1998). Wheat or rice straw is the most commonly used non-wood fiber raw material. Straw yields short-fibre pulp, which is similar to hardwood pulp. The high silica content is typical of non-wood materials (Myréen 2000).

1.2 Technology and final product

Pulping and bleaching technology must be matched with the quality and characteristics of the pulp and paper grades to be produced. No single pulping or bleaching process can produce pulp suitable for all uses. For instance, newsprint is a high-volume product of moderate strength, opacity and printability, and it has 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 the natural brightness of the pulps. On the other hand, packaging papers need strength if they are to be usable: here it is necessary to accept a lower yield via a different manufacturing route in order to obtain this strength, but once again the bleaching requirement may be low. The level of delignification and bleaching applied needs to be high in the case of writing and printing papers as well as outer packaging boards – their brightness and durability need to last for years without yellowing. The amount of effort required in bleaching can therefore vary widely.

2. Process description

2.1 Pulping methods applied

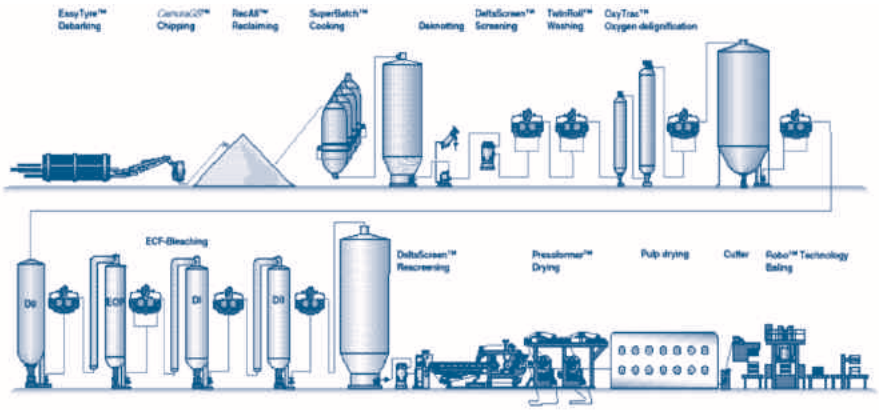
The main processes involved in making pulp and paper products are raw material handling and preparation, storage (and preservation for non-woods), wood debarking, chipping and agricultural residue cleaning, deknotting, pulping, pulp processing and bleaching if required and, finally, paper or paperboard manufacturing.

The manufacture of pulp utilizes mechanical, thermomechanical, chemimechanical and chemical methods. Mechanical pulping processes use grinding for logs and disc refiners

for chips. In these 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. The first step is followed by secondary disc refining and direct supply to a paper machine. Mechanical pulps can often be used without bleaching, but where brightening is applied it is achieved using compounds such as dithionite or peroxides (Gullichsen and Fogelholm 2000).

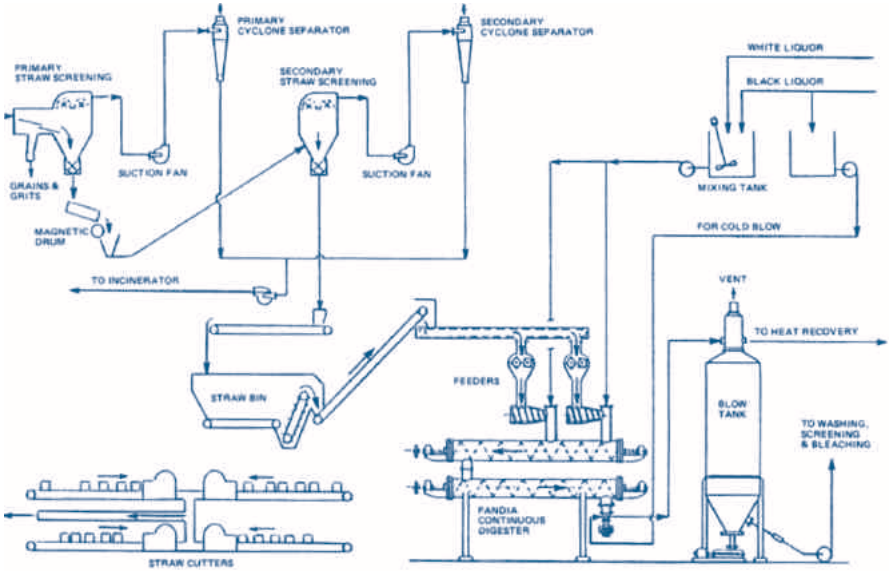
Lignin binds the fibres in the wood structure. In chemical pulping, the release of fibres is facilitated by chemicals that dissolve lignin. The lignin and many other organic substances are thus put into solution. This occurs in pressure vessels, called digesters, which are heated, pressurized vertical stationary vessels for wood-based raw material. Spherical rotary digesters or tumbling cylindrical digesters are used in batch pulping systems in various chemical processes for non-woods. In Figures 2 and 3, typical flow diagrams for wood-based and non-wood-based processes are presented. The residual lignin in fibres is removed by bleaching with chemical reagents. Some attempts to use enzymes have been introduced to enhance the effect of chemicals. Loss of yield, impacts on fibre properties and increased costs set limits to wider use of enzymes.

Figure 2. Typical flow diagram for modern kraft pulping process with ECF bleaching



Source: Metso Automation Inc.

Figure 3. Typical flow diagram for wheat straw pulping using the Pandia continuous digester system



The main chemical, semi-chemical and chemimechanical pulping techniques are as follows:

- Sulphate (kraft) uses a mixture of sodium hydroxide and sodium sulphide under alkaline conditions to dissolve the lignin from 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 lignin; most wood fibres (chemical and semi-chemical methods);
- Lime, lime-soda: In particular, non-wood fibres;
- Cold soda uses sodium hydroxide pretreatment at ambient temperatures, alone or with sodium carbonate: In particular, hardwood and non-wood fibres (semi-chemical);
- Soda anthraquinone (AQ): Sodium hydroxide alone or with sodium carbonate and a catalyst anthraquinone; hardwood and non-wood fibres (chemical, similar to kraft but without sulphur), reduced odour;
- Organosolv methods: Wood and non-wood applications, some proven at mill scale but only one process is available commercially.

The kraft or sulphate process is the dominating pulping process worldwide, constituting 84% of the world's chemical pulp production and 63% of total chemical and mechanical pulp production.

Non-wood pulps are almost exclusively produced using chemical and semi-chemical processes. Of the chemical pulping methods applied to non-wood materials, the soda process is the most important, followed by the kraft process and the neutral sulphite process. Mills based on traditional lime and lime-soda processes are still in operation (Edelman et al. 2000; *Proceedings* 1992). Many new processes for non-wood pulping are under investigation.

2.1.1 The kraft (sulphate) pulping process

The kraft process uses a sodium-based alkaline pulping solution consisting of sodium sulphide (Na_2S) and sodium hydroxide (NaOH). The fibres are liberated in the cooking plant by dissolving the lignin and part of the hemicellulose in the cooking chemical solution (white liquor). 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 and, at bleached mills, the substances dissolved during bleaching and the residues of the bleaching chemicals. Many small mills do not recover the liquor.

The recovery of non-wood fibre liquors is problematic due to the high silica content of fibre materials and rapid increase of the liquor viscosity during evaporation, as well as difficulties in achieving high solids content in the concentrated liquor fed to the recovery system. However, this area of recovery technology is currently receiving considerable attention with some claims for viable processes.

2.1.2 Lime and soda processes

These are processes that use 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 and bleaching chemicals remain in the wastewater, apart from the volatiles incidentally released to the atmosphere. The delignification ability is inadequate for producing wood-based pulps with low yield and high brightness. 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 causticization of the sodium carbonate smelt. After cooking, pulps that are not to be bleached are refined to separate the fibres.

2.1.3 Sulphite pulping processes

The sulphite pulping process is based on aqueous sulphur dioxide and a base – calcium, sodium, magnesium or ammonium. This method is losing its importance and only 10% of the world's pulp is produced with 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. Compared to kraft pulps, sulphite pulps are relatively bright and are also relatively easy to bleach with oxygen-based chemicals, such as peroxides.

2.1.4 Solvent-based processes

Solvent-based pulping processes can be used for both wood and non-wood raw materials. These organosolv pulping processes use the following solvents, amongst others: formic acid, peroxyformic acid, acetic acid, ethanol, methanol and acetone (Rousu and Antila 2002; Laxén and Halttunen 1992; Stern 2003; Edelman et al. 2000). Most alcohol and acidic cooking methods are sulphur-free processes and they produce readily bleachable pulp. Some solvent-based cooking methods are better suited for hardwood (e.g. Alcell) and some for both hardwood and softwood raw materials (e.g. NAEM, Organocell, Acetocell, Formacell and ASAM). However, none of these suggested techniques has been proven to be feasible in commercial operation, and the pilot production lines have been shut down. The applicability of solvent-based pulping for non-wood material has been studied (e.g. Alcell, Milox, Chempolis). When compared to traditional kraft non-wood pulping some laboratory-scale experiments show that the yield of the non-wood organosolv pulps is higher using ethanol-soda, ASAM and Organocell processes (Shatalov and Pereira 2005). The pilot-scale processes of Milox, Formacell, and ASAM produce pulps that are best for bleachability (Gullichsen and Fogelholm 2000).

2.2 Bleaching

Bleaching after pulping is a chemical process applied to pulps in order to increase their brightness. To reach the required brightness level, bleaching should be performed by removing the residual lignin of chemical pulps (delignifying or lignin-removing bleaching). All lignin cannot be removed selectively enough in a single bleaching stage, but pulp is usually bleached in three to six stages. The first two stages primarily release and extract lignin, and the subsequent stages remove the lignin residues and finish the product. These bleaching sequences are applied to maximize the bleaching effect of each component. Water is used to perform intermediate washes to remove extracted waste from the pulp (Gullichsen and Fogelholm 2000; Stenius 2000). The commonly applied chemical treatments in bleaching, and their abbreviated designations, are shown in Table 1.

Table 1. Commonly applied chemical treatments in bleaching

Treatment	Abbreviation	Description
Chlorination	C	Reaction with elemental chlorine in acidic medium
Alkaline extraction	E	Dissolution of reaction products with NaOH
Hypochlorite	H	Reaction with hypochlorite in alkaline medium
Chlorine dioxide	D	Reaction with chlorine dioxide (ClO_2)
Chlorine and chlorine dioxide	CD	Chlorine dioxide is added in chlorine stage
Oxygen	O	Reaction with molecular oxygen at high pressure in alkaline medium
Extraction with oxygen	EO	Alkaline extraction with oxygen
Peroxide	P	Reaction with hydrogen peroxide (H_2O_2) in alkaline medium
Chelating	Q	Reaction with chelating agent EDTA or DTPA in acidic medium for removal of metals
Ozone	Z	Ozone using gaseous ozone (O_3)

If molecular chlorine and hypochlorite are excluded, the term applied for the bleaching sequence is chlorine dioxide bleaching or elemental chlorine-free (ECF) bleaching. If the sequence only uses oxygen-based chemicals, such as oxygen, ozone, alkaline or acidic peroxide, the terms oxygen chemical bleaching or totally chlorine-free (TCF) bleaching can be used.

For softwood kraft pulps, a number of bleach sequences utilizing four to six stages are commonly used to achieve full-bleach brightness (level 89–91%). Bleaching sequences (full brightness) like CEHDED and CEDED were in operation in the 1960s and 1970s. Sequences more typical of modern mills are OD(EOP)D, OD(EOP)DP, Q(PO)DD, Q(PO)(DQ)(PO) and (Z(EO))DD (full brightness).

With an oxygen delignification stage or reinforced extraction stage, the bleaching sequences could be as follows: O(D+C)(EO)D; O(CD)EDED; and O(D)(EO)DED.

Hardwoods are easier to bleach due to their lower lignin content. Furthermore, less bleaching effort is required for sulphite pulps due to higher prebleach brightness.

For both non-wood and wood raw material, the pulping process removes some of the lignin. After pulping a variety of chemicals and catalysts can be used to remove lignin. Traditionally these chemicals have included gaseous chlorine and chlorine dioxide. For non-wood pulps, one-stage hypochlorite bleaching or conventional four-stage

bleaching (CEHH, CEHD) is still very commonly used, depending on the final brightness requirements (Zheng et al. 1997). More recently, pressurized oxygen, ozone and hydrogen peroxide have been employed (Stern 2003).

2.2.1 Bleaching with elemental chlorine and hypochlorous acid

Elemental chlorine and hypochlorous acid are electrophilic bleaching chemical agents that react with all unsaturated structures, namely lignin structures; with polysaccharide degradation products, such as hexenuronic acid; and with extractive structures that contain carbon-carbon double bonds. These electrophilic bleaching agents are able to react with different unsubstituted aromatic carbon atoms in lignin to:

a. Chlorinate (when the carbon is not bonded with an oxygen atom); or

b. Chlorinate and depolymerize (via displacement of an -hydroxyl group); or

c. Merely depolymerize without chlorination (via hydroxylation).

These chlorination or depolymerization reactions make lignin alkaline soluble, and it can be removed from pulp in the alkaline bleaching stages of the bleaching sequence.

2.2.2 Formation of 2,3,7,8-TCDD/TCDF

Most of the formation of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) and 2,3,7,8- tetrachlorodibenzofuran (2,3,7,8-TCDF) is generated in the C-stage via the reaction of chlorine with the precursor of TCDD, namely dibenzo-*p*-dioxin (DBD), and with the precursor of TCDF, which is unchlorinated dibenzofuran (DBF). When these precursors are chlorinated, the key reaction is electrophilic aromatic substitution. The rate of this reaction will depend both on the concentration of the precursor and the concentration of chlorine. The levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF are not determined by the content of the lignin in pulp (Berry et al. 1989).

The chlorination of non-aromatic structures, such as hexenuronic acid, does not lead to the formation of polychlorinated aromatic degradation products.

The unchlorinated dioxin precursors are prevalent in certain mineral oils, which are part of some defoamer formulations used in the pulp and paper industry and are the major source of precursors. Wood itself may act as the source of dioxin precursor. Compression wood in particular contains higher concentrations of precursors than normal wood. The compression of wood also entails higher levels of coumaryl-type lignin, which may be a source of DBD- and DBF-like precursors.

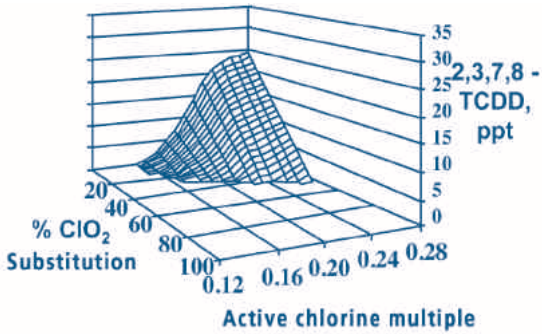
2.2.3 Elimination mechanisms for 2,3,7,8-TCDD/TCDF

Preventing the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF in the bleaching can be achieved mainly by using totally chlorine-free bleaching method and virtual elimination can be achieved by decreasing the amount of chlorine used in the first bleaching stage. This can be accomplished by reducing the atomic chlorine multiple by improving washing prior to chlorination, by using an oxygen and peroxide-reinforced extraction stage, and by increasing ClO_2 substitution (Rappe et al. 1989; Tana and Lehtinen 1996). The formation of 2,3,7,8-TCDF and 2,3,7,8-TCDD will be reduced by increasing ClO_2

substitution, as demonstrated in Figures 1 and 4. When the ClO_2 substitution level is higher than 85%, 2,3,7,8-TCDF and 2,3,7,8-TCDD can be virtually eliminated.

The summary effect of active chlorine multiple[1] and the ClO_2 substitution level can be seen in Figure 4. The level of dioxin formation under these conditions, i.e., high active chlorine multiple and low ClO_2 substitution, is expected to vary, depending on the DBD content of the brownstock.

Figure 4. Effect of active chlorine multiple and chlorine dioxide substitution level on 2,3,7,8-TCDD formation



Elemental chlorine can be completely replaced by ClO_2 (elemental chlorine-free bleaching). In this process ClO_2 is usually the main bleaching agent. The elemental chlorine can be replaced with ClO_2 in the first bleaching stage because the ClO_2 per chlorine atom has fivefold oxidation power compared with chlorine and it has practically the same selective lignin removal properties. Reinforcing the alkaline extraction stages in bleaching with oxygen and/or hydrogen peroxide results in an enhanced oxidizing bleaching effect, which reduces the residual lignin content of the pulp before the final ClO_2 bleaching stages. Increasing the degree of ClO_2 substitution decreases the formation of chlorinated organic substances and eliminates the formation of dioxins and furans. The increased substitution of chlorine by ClO_2 generally requires modifications in the bleaching process and also expansion of the on-site chlorine dioxide plant.

The elemental chlorine-free bleaching process is different for softwood and hardwood, and in existing mills the possibilities of the concept are tied to the current bleaching process. Generally, to reach a certain brightness target hardwood requires fewer chemicals than softwood, which usually means that the number of bleaching stages can be reduced. Over the years the dosage of chlorine dioxide has decreased in hardwood bleaching by one-third as it has been substituted by oxygen-based chemicals. Examples for light elemental chlorine-free bleaching sequences are (DZ)(EOP)D, (DQ)(PO) and D(EOP)D(PO). These can be applied for both hardwood and softwood, depending on the brightness target (European Commission 2000).[2]

Small amounts of chlorine are formed as a by-product in chlorine dioxide generation systems. Part of this molecular chlorine impurity will be present when chlorine dioxide is used as a bleaching reagent. There are several chlorine dioxide preparation processes

available producing different amounts of elemental chlorine as by-product. Therefore a careful selection of the chlorine dioxide generation method will decrease the formation of molecular chlorine impurities and the unintentional formation of dioxins.

Elemental chlorine-free pulp (kraft pulp) bleached with ClO_2 holds the predominant position within the industry, accounting for roughly three-quarters of the bleached pulp produced worldwide.

3. Best available techniques for production of pulp using elemental chlorine

3.1 Primary measures

The principal best available techniques for minimizing or eliminating the formation of 2,3,7,8-TCDD/TCDF in wood and non-wood bleaching processes are as follows:

- Reduction of the application of elemental chlorine by decreasing the multiple or increasing the substitution of ClO_2 for molecular chlorine;
- Elimination of elemental chlorine by replacing it with ClO_2 (elemental chlorine-free bleaching) or with chlorine-free chemicals;
- Utilization of DBD- and DBF-free defoamers;
- Prevention of using non-wood raw material (reeds) that are contaminated or potentially contaminated by PCDD/PCDF as impurities in sodium pentachlorophenolate (Zheng 1997)
- Effective brownstock washing to enable the reduction of chlorine multiple;
- Maximization of knot and dirt removal to enable the reduction of chlorine multiple;
- Elimination of the pulping of furnish contaminated with polychlorinated phenols.

3.2 Secondary measures

The following general measures are suggested:

- 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;
- Investment planning/cycles: Coordination of process improvements to reduce technical bottleneck delays in the introduction of better techniques;
- Training, education and motivation of personnel: Training staff can be a very cost-effective way of reducing discharges of harmful substances;
- Process control monitoring and optimization: To be able to reduce different pollutants simultaneously and to maintain low releases, improved process control

is required, including raw materials specification and monitoring of raw materials for precursor materials;

- Adequate maintenance: To maintain the efficiency of the process and the associated abatement techniques at a high level, sufficient maintenance has to be ensured;
- Environmental management system: A system that clearly defines the responsibilities for environmentally relevant aspects in a mill. It raises awareness and includes goals and measures, process and job instructions, checklists and other relevant documentation, and incorporation of environmental issues into process change controls;
- Development of environmental monitoring and standard monitoring protocols, including release monitoring for new facilities.

4. Alternatives

4.1 Totally chlorine-free bleaching for kraft pulp

The totally chlorine-free (TCF) process developed rapidly in the 1990s but has gradually lost its attraction because of its weaknesses in fibre characteristics, lower pulp yield and higher energy consumption. The elemental chlorine-free (ECF) process has taken over as the leading bleaching method. Some TCF processes have started to lose their shares in the market and a number of TCF mills are converting to ECF pulp production. The operating costs of TCF pulping are usually higher than those of ECF pulping due to the higher chemical costs required to reach the same level of pulp brightness.

TCF bleaching is a bleaching process carried out without any chlorine-containing chemicals. In this process, hydrogen peroxide together with ozone or peracetic acid are the most commonly used chemicals. Ozone has become the most common complement to peroxide in TCF bleaching sequences. The main purpose of using ozone is to provide more delignification power. Provided that the pulp has a low enough kappa number[3] after extended cooking and oxygen delignification and that transition metals (e.g. Mn_2^+) have been removed in the necessary chelating stages (Q-stages), it is possible to attain full market brightness with peroxide as a the sole bleaching chemical.

Examples for different TCF bleaching sequences are listed below:

Softwood	**Hardwood**
Q(EP)(EP)(EP)	QPZP
Q(OP)(ZQ)(PO)	Q(OP)(ZQ)(PO)
Q(EOP)Q(PO)	Q(EOP)Q(PO)
Q(OP)ZQ(PO)	Q(OP)ZQ(PO)

Notes:

Q = Acid stage where chelating agent EDTA or DTPA has been used for removal of metals.

EP = Extraction stage using NaOH with subsequent addition of H_2O_2 solution as a reinforcing agent.

EOP = Alkaline extraction bleaching stage using sodium hydroxide with subsequent addition of oxygen and hydrogen peroxide solution as a reinforcing agent.

EO = Extraction stage using NaOH with subsequent addition of gaseous oxygen as a reinforcing agent.

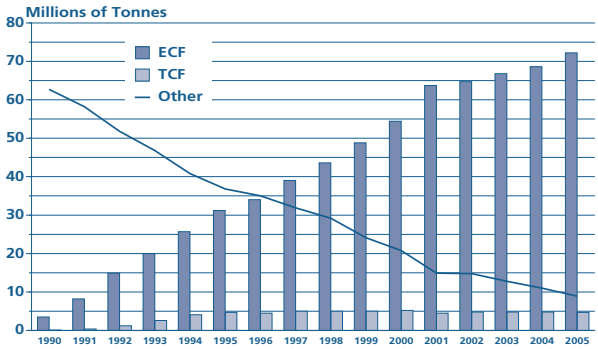
P = Alkaline stage with H_2O_2 as liquid.

Z = Ozone bleaching using gaseous O_3.

PO = Pressurized peroxide bleaching.

The trends of total chemical pulp production in the world are demonstrated in Figure 5. TCF kraft and sulphite pulp accounts for less than 5% of production and is primarily produced in Northern and Central Europe.

Figure 5. Trends in bleached chemical pulp production: World, excluding China and India.



Note: "Other" refers to pulp bleached with some molecular chlorine.

4.2 TCF bleaching for non-wood pulp

Because of their poor bleachability, non-wood pulps cannot be satisfactorily bleached without chlorine chemicals if the traditional alkaline non-wood process is used. Non-wood materials also contain notable amounts of metal ions, including potassium, calcium, manganese, copper and iron. When the pulp is bleached without chlorine chemicals the transition elements form radicals, which react unselectively with the pulp, causing a loss of yield and strength properties. Chelates are often added in the initial stages of bleaching to reduce the quantity of metals in the fibre. Furthermore, bleaching is accompanied by the formation of oxalic acid. Calcium reacts with oxalic acid into

calcium oxalate, which deposits easily. Due to this, TCF bleaching is not viable in traditional alkaline non-wood processes. There is continuous research on TCF bleaching in solvent-based processes.

5. Achievable performance levels associated with best available techniques and best environmental practices

When the ClO_2 substitution level is higher than 85% in traditional bleaching, or if ECF bleaching or TCF bleaching is used, emissions of 2,3,7,8-TCDF and 2,3,7,8-TCDD to water are lower than the limit of quantification using EPA Method 1613 (refer to table 2).

5.1 Performance reporting

Performance reporting is recommended as described in section III.C (vi) of the present guidelines.

Where emissions testing is not possible (for example, analytical capacity is not readily available), the use of PCDD/PCDF release 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 in section 6.7.1 of the UNEP *Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases* (UNEP 2003).

5.2 Performance standards

Table 2 summarizes the existing performance standards applied to pulp mills.

Table 2. Summary of existing performance standards applied to pulp mills

New plant	2,3,7,8-TCDD/TCDF pg/l to water	2,3,7,8-TCDD/TCDF ng/kg to sludge	Defoamers DBD and DBF mg/kg
Canada – Federal[a]	Lower than quantification level in treated final effluent		DBD <10 DBF <40
USA kraft and soda[b]	2,3,7,8-TCDD <10 2,3,7,8-TCDF ≤ 31.9 in bleach plant effluent	10/100	
USA ammonium-based and speciality sulphite[b]	2,3,7,8-TCDD <10 2,3,7,8-TCDF <10 in bleach plant effluent		
Australia[c]	2,3,7,8-TCDD <15 in treated final effluent		
Tasmania, Australia[d]	2,3,7,8-TCDD <10 in treated final effluent		
Japan[e]	<10 pg TEQ/L		

Sources:

a. Government of Canada. 1992. *Canadian Pulp and Paper Mill Defoamer and Wood Chip Regulations*. SOR/92-268. Canadian Department of Justice. www.ec.gc.ca/NOPP/DIVISION/EN/detail.cfm?par_docID=99.

b. United States Congress, Office of Technology Assessment. 1989. *Technologies for Reducing Dioxin in the Manufacture of Bleached Wood Pulp*. OTA-BP-O-54. United States Government Printing Office, Washington, D.C. govinfo.library.unt.edu/ota/Ota_2/DATA/1989/8931.PDF.

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d. Resource Planning and Development Commission. 2004. *Development of New Environmental Emission Limit Guidelines for Any New Bleached Eucalypt Kraft Pulp Mill in Tasmania.* Government of Tasmania, Australia. http://www.rpdc.tas.gov.au/BEKM/pages/bekm.htm.

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Notes

[1] The term active chlorine multiple means the amount of active or equivalent chlorine expressed as a percentage on oven dry unbleached pulp divided by the unbleached pulp kappa number.

[2] See table 1 for designations.

[3] The kappa number is an indirect measure of the residual lignin content in a pulp measured via the consumption of an oxidant chemical (for example, potassium permanganate).

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