# Section V

# Guidance/guidelines by source category: Source categories in Part II of Annex C

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# Part II Source category (c):

# Production of pulp using elemental chlorine or chemicals generating elemental chlorine

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# Glossary

**(active) Chlorine multiple:** is defined as the amount of active or equivalent chlorine expressed as a percentage on oven dry unbleached pulp divided by the unbleached pulp Kappa number, or $Cl_2$ multiple is the ratio of chlorine to lignin content.

**Elemental chlorine free (ECF):** is a technique that uses chlorine dioxide ($ClO_2$) for the bleaching of wood pulp. It does not use elemental chlorine gas ($Cl_2$) during the bleaching process.

**GE brightness:** is used for specification of paper brightness primarily in North America. The Technical Association of the Pulp and Paper Industry (TAPPI) has authorized method T 452 (TAPPI 2023) for use in determining the brightness of paper. TAPPI T 452 brightness is often referred to as GE brightness since General Electric invented one of the first paper brightness testing machines which became the industry standard for decades. The ISO paper brightness measurement system, as defined by ISO 2470-1 (ISO 2016) and ISO 2470-2 (ISO 2008), is used for specification of paper brightness throughout Europe and in many other parts of the world.

**Hardwood:** Group of wood species including, e.g., aspen, beech, birch and eucalyptus.

**Kappa number:** The Kappa number is an indirect measure of the residual lignin content in a pulp sample measured via the consumption of an oxidant chemical (for example, potassium permanganate).

**Softwood:** Wood from conifers including, e.g., pine and spruce.

**Sulfate (or Kraft) process**: pulp produced by cooking wood chips in pressure vessels in the presence of a sodium hydroxide and sodium sulphide ($Na_2S$) liquor. The pulp may be unbleached or bleached. End uses are widespread, with bleached pulp particularly used for graphic papers, tissue and carton boards. Unbleached pulp is commonly used in liner for corrugated board, wrappings, sack and bag papers, envelopes and other unbleached specialty papers.

**Sulfite (or bisulfite) process**: pulp produced by cooking wood chips in a pressure vessel in the presence of bisulfite liquor. End uses range from printing and writing papers to tissue, sanitary papers, textiles and various chemicals (dissolving pulps, e.g., viscose for the production of rayon, pure cellulose for food additives, etc.).

**Totally chlorine-free (TCF):** bleaching technique uses oxygen delignification in combination with hydrogen peroxide or ozone as the main bleaching agents.

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

## Summary

Formation and occurrence of polychlorinated dibenzo-p-dioxins and/or polychlorinated dibenzofurans (PCDD/PCDF) are associated with the use of elemental chlorine ($Cl_2$) in the chemical bleaching step during the production of pulp. Other process steps in the production of pulp do not generate measurable amounts of PCDD/PCDF.

Specifically, of the 17 PCDD/PCDF congeners with chlorine in the 2,3,7 and 8 positions, mainly two congeners – 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 marker compounds being produced during pulp bleaching using elemental chlorine. Most of the formation of the 2,3,7,8-TCDD and 2,3,7,8-TCDF is generated in the chlorination stage with elemental chlorine (C-stage) when chlorine reacts with precursors of TCDD and TCDF. Historically, high values of these congeners were observed when elemental chlorine ($Cl_2$) was applied in the first stage of chemical bleaching.

With respect to the bleaching agent, Totally Chlorine-Free bleaching (TCF) and Elemental Chlorine-Free bleaching (ECF; i.e., use of chlorine dioxide ($ClO_2$)) are considered BAT.

The principal best available techniques for minimizing or eliminating the formation of PCDD/PCDF in wood and non-wood bleaching processes during pulp production are as follows:

- For new and existing sources: use of $ClO_2$ (ECF) or chlorine-free chemicals (TCF) for bleaching
- For existing sources that currently use elemental chlorine: elimination/phase-out of elemental chlorine by replacing it with $ClO_2$ (elemental chlorine-free bleaching) or with chlorine-free chemicals.

  During this phase-out process the following measures are to be applied:
    - reduction of the application of elemental chlorine by decreasing the multiple or increasing the substitution of $ClO_2$ for elemental chlorine;
    - effective brownstock washing to enable the reduction of chlorine multiple;
- Utilization of dibenzo-p-dioxin (DBD)-free and dibenzofuran (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 et al., 1997).

The global production data for bleached chemical pulp in 2005 already showed that most elemental chlorine bleaching has been substituted mainly by ECF bleaching accounting for 85% of the pulp produced and partly by TCF bleaching accounting for 5% of the pulp produced (Alliance for Environmental Technology, 2005; Figure).

# 1 INTRODUCTION

1. 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) (UNEP, 2001) and more recently, pentachlorobenzene (PeCB) (UNEP, 2009), polychlorinated naphthalenes (PCN) (UNEP, 2015), and hexachlorobutadiene (HCBD) (UNEP, 2017). While a wide range of studies for PCDD/PCDF release has been published (e.g., Swanson et al., 1988; Fiedler et al., 1990; USEPA, 1990; Berry et al., 1991), there is a lack of data of release of other unintentional POPs by the pulp and paper industry. In accordance with the

recommendation from the UNEP Toolkit (UNEP 2013), measures to reduce or eliminate unintentional POPs formation, efforts should target PCDD/PCDF which also will result in the reduction of other unintentional POPs. Therefore, this section addresses formation, occurrence, reduction or elimination of PCDD/PCDF as marker compounds for the application of BAT/BEP for unintentional POPs. For information on other POPs, relevant scientific literature should be consulted.

2. 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, and residues sent to landfill. This guideline addresses the process of pulp making and PCDD/PCDF formation and release in the bleaching steps using chlorine and in other processes.

## 1.1 History/Background

3. In the 1980s/1990s, there was a shift from traditional concerns associated with the pulp and paper manufacture from oxygen deficiency, fibre deposition, or impacts on fish living in receiving waters towards impacts from substances that were later designated as POPs. Whereas the conventional concerns were addressed by regulatory measures such as limit values on biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), and acute toxicity to fish, newly introduced regulatory measures included limits on overall discharges of chlorinated organic materials. These discharges were quantified with a generic, non-specific parameter, namely 'adsorbable organically-bound halogens (AOX) (Berry *et al.*, 1991). The chemicals of greatest concern were PCDD and PCDF, especially, 2,3,7,8-TCDD and 2,3,7,8-TCDF, which constituted only a very minor fraction of 0.1 % of the AOX (Berry *et al.*, 1991). Other chlorinated substances, such as chloroform or chlorophenols are formed as well and are indicated by AOX (Juuti et al. 1996; Nakamata et al. 2004; Correa et al. 2003). Consequently, AOX compounds do not correlate with PCDD or PCDF nor with the dioxin toxic equivalents (TEQs) and therefore, AOX determination is not a suitable parameter for PCDD/PCDF control but of the overall release of chlorinated organics.

### 1.1.1 Early findings of PCDD/PCDF in pulp and paper production

4. Initial concerns of dioxin contamination from chlorine bleaching in the pulp and paper industry relates to the presence of mainly two of the 17 2,3,7,8-substituted PCDD/PCDF, namely 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF). These two isomers among the TCDD and the TCDF are more prominent in the chemical bleaching processes than in a typical incineration pattern (see Figure 1). In addition, the formation of 1,2,7,8-TCDF, which is not included in the 2005 World Health Organization Toxicity Equivalency Factors (WHO2005-TEF) scheme and not routinely analyzed by dioxin laboratories (Van den Berg et al., 2006), is an indicator of $Cl_2$ use in chemical bleaching of pulp (see Figure 2). These three "indicator" PCDD/PCDF were found in pulp (cellulose), paper, and in effluents and sludges (Fiedler et al., 1990). They were especially found in products and residues from pulp mills using elemental chlorine ($Cl_2$) as the bleaching agent. Subsequently, early reports and controls assessed TCDF and TCDD only (Amendola et al., 1989; Whittemore et al., 1990; USEPA, 1990). In the mid-1980s the discovery of PCDD and PCDF 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 comprehensive international research showed that the principal mechanism for formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF is generated in the chlorination stage (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). 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., 1991).

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

6. 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.

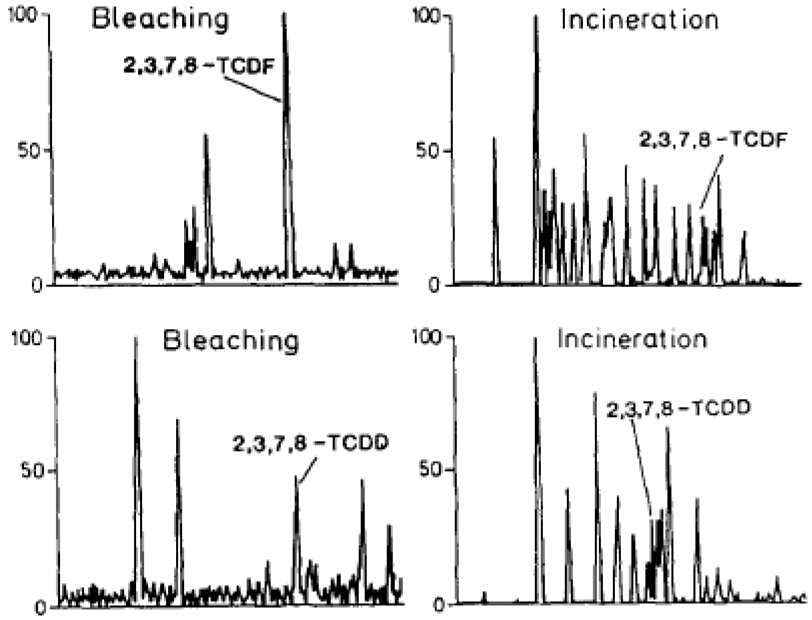

Figure 1: Comparison of TCDD and PCDF isomers in samples from spent bleach liquor “Bleaching” and from incineration “Incineration” (figure from (Swanson *et al.*, 1988))

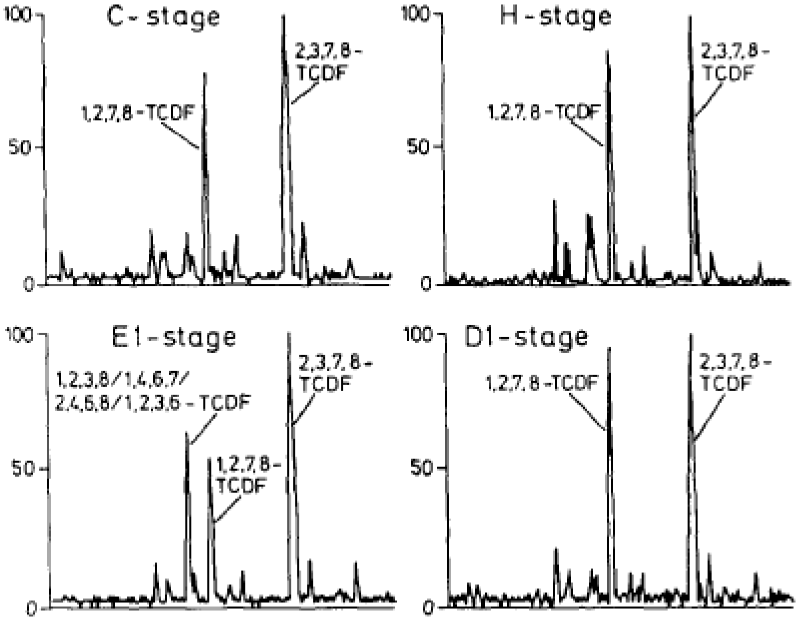

Figure 2: TCDF isomers in samples from the four bleaching steps (figure from Swanson *et al.*, 1988). See Chapter 2.1.2 for more details on the bleaching steps (stages).

7. The chromatograms shown in Figure 2 were from samples taken from a pulp mill producing 850 t/d of bleached softwood (pine) Kraft pulp. The pulp was semi- or fully bleached using a conventional bleaching sequence including C (elemental chlorine), E (alkaline extraction), H (hypochlorite), D (chlorine dioxide), and (C+D) EOHD$_1$ED$_2$ steps (Swanson *et al.*, 1988).

## 1.1.2 Trends in World Chemical Bleached Pulp Production

8. The use of elemental chlorine in chemical bleaching of pulp has been largely replaced by chlorine dioxide and other oxygen-based chemicals such as molecular oxide, peroxide and ozone (Powell, 1997) but regional differences might still exist (Figure 3). A bleaching process using chlorine dioxide or other chlorinated chemicals, but not elemental chlorine, is referred to as 'elemental chlorine-free' (ECF) and a process that does not use any chlorinated chemicals is referred to as 'totally chlorine-free' (TCF). In 2005, pulp produced utilizing ECF production accounted for nearly 85% of world market share. In contrast, TCF (Totally Chlorine-Free) production maintained a small niche market at less than 5% of world bleached chemical pulp production. Regional differences exist and elemental chlorine was still used to bleach pulp in 2005 in different regions (Alliance for Environmental Technology, 2005) and in 2023 still share of e.g. the India pulp and paper production (3 of the 28 larger pulp and paper companies and likely the 800 smaller pulp and paper industries) (Kumar, 2024).

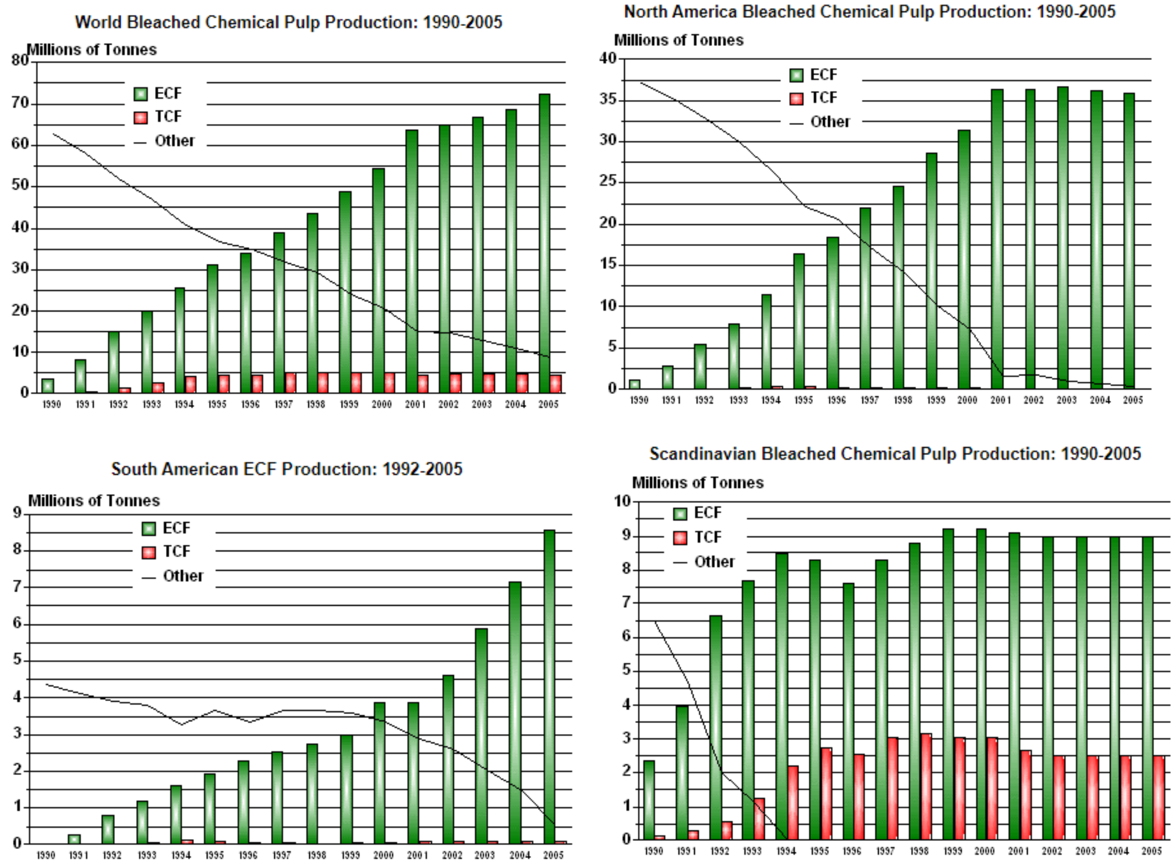

Figure 3: Overview of bleached chemical pulp production from 1990-2005. Green bars denote pulp bleached utilizing Elemental Chlorine-Free (ECF) technology, red bars denote pulp bleached with TCF (Totally Chlorine-Free) technology, and the black line denotes pulp production utilizing other bleaching technology, including elemental chlorine (Alliance for Environmental Technology, 2005)

# 2 PROCESS DESCRIPTION OVERVIEWS FOR PRODUCING PULP AND FOR CHEMICAL BLEACHING OF PULP

## 2.1 Raw materials for pulp

9. Pulp and paper are manufactured from three main raw material groups: wood, non-wood (i.e., rice straws, corn stalks, cotton stalks, bagasse) and recycled wastepaper (Abd El-Sayed et al., 2020). Globally (data for 2018), pulp is mainly made from wood (63 %), recycled wastepaper (34 %) and non-wood sources (3%) (Ferdous et al., 2020). It must be mentioned that the shares differ widely by country/region. In 2022, the production capacity of chemical wood pulp, sulfate bleached was about 133 million tons in selected countries (FAO, 2022). Largest producing countries are Brazil (17% production share), USA (15%), Mainland China (13%) and Indonesia (6%). Pulp from fibers other than wood production for 2022 was reported as 11.6 million tons, with Mainland China (48% share), India (26% share) being the largest producing countries (FAO, 2022).

## 2.2 Pulping processes

10. Pulp is produced by several techniques, which yield different products and by-products. They are typically grouped into mechanical and chemical pulping. Mechanical pulping involves conversion of wood into fibres by physical or mechanical grinding, aided in some cases by heat, high pressure and/or chemicals. Mechanical pulping is not in-scope here because such pulps are not bleached.

11. In the chemical pulping process, the fibres are liberated from the wood matrix as the lignin is removed by dissolving it into the cooking chemical solution at a high temperature. Part of the hemicellulose is dissolved as well in the cooking. Mainly two processes exist for wood: the sulfite process and the Kraft (sulfate) process. The latter process dominates/dominated the industry because it more easily allows recovery of valuable chemicals and, as a result, minimizes discharges into the environment (Tana and Lehtinen, 1996; European Union *et al.*, 2015). Non-wood raw materials may be pulped using the alkaline process.

12. Neither the Kraft nor the sulfite process is able to remove all lignin; 5 %-10 % of the original lignin remains in the pulp. Removal of the residual lignin requires a multi-stage bleaching process.

13. Alkaline pulping was developed for wood materials but has been applied in the non-wood fiber cooking process. Accordingly, the aqueous solution of the alkaline chemical agent, e.g., NaOH or $Na_2CO_3$ in the caustic soda process, would be utilized to treat fibre materials to dissolve most of the lignin and separate the fibres from the material into pulp. The cooking agents in the alkaline pulping process [of non-wood] can be divided into oxygen alkali method, sulfate method, caustic soda method, lime method, and others.

14. The caustic soda pulping process has been widely used in the pulping of non-wood raw material. The dosage NaOH or $Na_2CO_3$ depends on the fibre properties. Cooking temperature is, essentially, cooking time and alkali charge which refers to the amount of the active alkali dosage. Generally, the alkali charge is around 16 %, and the cooking temperature is 140 °C–170 °C (Ferdous *et al.*, 2020).

15. The Kraft process is the principal chemical pulping process worldwide due to the superior pulp strength properties compared with the sulfite process, its applicability to all wood species, as well as to the efficient chemical recovery systems that have been developed and implemented. The Kraft process accounts for approximately 80 % of the world pulp production, while the sulfite process accounts for ca. 10 % of world production. (European Union *et al.*, 2015).

## 2.3 Purpose of Bleaching Pulp

16. Wood pulp fibres are bleached before paper making to reduce or remove lignin and resin in order to produce white paper and to improve the ability of the paper to withstand degradation, which may cause the paper to turn yellow. Bleaching results in paper that has clean, white, and bright characteristics. Bleaching also sterilises the pulp and eliminates taste and odour for use in demanding applications, such as food packaging (Stora, 2017).

17. 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.

## 2.4 Bleaching processes

18. Bleaching of pulp is performed in several bleaching sequences to achieve the desired bleaching action. Different chemicals are used in each stage usually with washing between two stages. The preference of bleaching sequences depends on many parameters such as pulp categories, environment issue, operating cost, and product quality of final bleached pulp.

19. For softwood pulps, bleaching was normally accomplished by successive treatment with elemental chlorine ($C_1$), alkali ($E_1$), chlorine dioxide ($D_1$), alkali ($E_2$), and chlorine dioxide ($D_2$). Often, a hypochlorite stage (H) was inserted between the $E_1$ and $D_1$ stages.

20. There are three principal bleaching processes:

- Chlorine: uses chlorine gas elemental/molecular chlorine and hypochlorite.
- Elemental chlorine-free (ECF): is a bleaching sequence utilizing chlorine dioxide (ClO2) is the main bleaching agent.
- Totally chlorine-free (TCF): is a bleaching process carried out without any chlorine-containing chemicals.

21. Please note, process chlorine-free (PCF) indicates that fibres are recycled and treated/bleached using totally chlorine-free compounds. For recycled fibre from used and unused recollected paper, cardboard and paperboard that is suitable and intended for reuse as fiber raw material specific techniques can be applied (cf. standard list of waste paper grades and their qualities; valid version of DIN EN 643). For example,

- By adding chlorine-free bleaching agents (mainly hydrogen peroxide, sodium dithionite), the recycled pulp is brightened. Fiber constituents can go into solution.
- In reductive bleaching, the chromophoric (color-forming) molecular structures are changed and thus decolorized.
- Oxidative bleaching with hydrogen peroxide makes the color-forming lignin residues more water-soluble and thus removable. In cases where alkalization with calcium or magnesium hydroxide is sufficient, 30% less leaching of organic matter (COD load) has been observed compared to caustic soda.

22. Recovered fibre cannot be considered totally chlorine free, because the previous bleaching method of the fibres is not known (Stora, 2017).

### 2.4.1 Definitions

23. Commonly used definitions and abbreviations are shown in Table 1.

Table 1: Definitions and abbreviations including steps in the pulping process (Goyal 2022)

| Symbol | Stage | Amount | Time | pH | Consistency | Temperature | Description |
|---|---|---|---|---|---|---|---|
| A | Acid wash | | | | | | To remove metal elements from pulp |
| B | Boron hydride $NaBH_4$ | | | | | | |
| C | Chlorination | 5%-7% on pulp | 40 min | 2 | 3%-4% | 20 °C -25 °C | Elemental chlorine ($Cl_2$) is an effective de-lignifying agent. As it breaks lignin bonds, it adds chlorine atoms to the lignin degradation products, thus producing significant amounts of chlorinated organic material. |
| D | Chlorine dioxide | 0.6%-1.0% on pulp | 180 min | 3.5 - 4.0 | 10% - 12% | 60 °C- 80 °C | Chlorine dioxide ($ClO_2$) is a highly selective chemical that can both de-lignify and brighten pulp. It oxidizes lignin but does not add chlorine atoms onto lignin fragments; however, small amounts of elemental chlorine and other chlorine compounds formed during the chlorine dioxide bleaching process react with degraded lignin to form chlorinated organic compounds. |
| CD, C/D or D/C | | | | | | | Chlorine and chlorine dioxide added together |
| E | Alkaline extraction | 3% -4% on pulp | 120 min | 12 | 10% - 20% | 45 °C- 95 °C | To remove colored components from partially bleached pulps that have been rendered soluble in dilute warm alkali solution. |
| $E_0$ | | | | | | | Alkali extraction reinforced with oxygen |
| $E_P$ | | | | | | | Alkali extraction reinforced with hydrogen peroxide |
| $E_{OP}$ | | | | | | | Alkali extraction reinforced with oxygen and hydrogen peroxide |
| F | Formamidine sulphinic acid | | | | | | |
| H | Sodium hypochlorite | 1% on pulp | | 11-11.5 | 3% - 15% | 30 °C- 60 °C | Sodium hypochlorite (NaOCl) is an inexpensive de-lignifying agent formed by mixing elemental chlorine with alkali at the mill. |
| M | Chlorine monoxide or hypochlorous | | | | | | |
| N | Nitrogen Compounds | | | | | | |
| O | Oxygen | 1.5%-2% on pulp | 60 min | 7 | 10%-15% | 85 °C- 95 °C | Oxygen removes lignin and modifies other coloring components. In the oxygen delignification/bleaching stage the pulp is treated with oxygen in a pressurized vessel at elevated temperature in an alkaline environment |

| Symbol | Stage | Amount | Time | pH | Consistency | Temperature | Description |
|---|---|---|---|---|---|---|---|
| P | Peroxide | 2-3% on pulp | 60-120 min |  | 10% - 30% | 65 °C- 80 °C | Hydrogen peroxide ($H_2O_2$) is mainly used to brighten pulps in the final bleaching stages. Peroxide is often used at the end of a conventional bleaching sequence to prevent the pulp from losing brightness over time. Preferred for mechanical and recycled fiber |
| $P_{aa}$ | Peracetic acid $CH_3COOOH$ |  |  |  |  |  |  |
| Q | Acid stage using Chelating agents |  |  |  |  |  | To control the brightness restricting and reversion effects of iron salts and other heavy metals in the pulp. |
| W | Wash |  |  |  |  |  | Pulp is washed almost every bleaching stage to remove reactants of preceding stage |
| X | Xylanese |  |  |  |  |  | Xylanase-based enzymatic pretreatment, in a TCF (Totally Chlorine-Free) sequence, results in easier bleaching and delignification of the pulp, causing a bleach-boosting effect |
| Y | Sodium hydrosulfite | 0.5%-1.2% on pulp | 35-60 min | 5.5 | 5%-8% | 60 °C-75 °C | Reductive bleaching. Good for recycled fibers |
| Z | Ozone | 0.1%-1-0% |  | 2.5 | 5%-15% | <65 °C | Ozone ($O_3$) is also an effective de-lignifying agent. It also brightens the pulp as well. Ozone attacks the cellulose fiber as well as the lignin |
| ZD |  |  |  |  |  |  | Ozone and chlorine dioxide added sequentially in same stage |

**Elemental chlorine ($Cl_2$)** was the bleaching agent of choice for many decades in the past due to its relatively low cost

**Chlorine dioxide ($ClO_2$)** has the highest selectivity among the technical bleaching agents. Bleaching with only $ClO_2$ in the first bleaching stage means that the total charge of effective chlorine has to be increased and oxygen and hydrogen peroxide are more extensively used in the extraction stages.

**Peroxide ($H_2O_2$)** can be applied in several process steps in both ECF and TCF.

**Ozone bleaching ($O_3$)** is used for both ECF and TCF pulps. The use of ozone is commonly used to produce hardwood pulps at high brightness.

**Oxygen bleaching** Extended delignification by (a) modified cooking or (b) oxygen delignification enhances the degree of delignification of pulp (lowering the kappa number) before bleaching and thus reduces the use of bleaching chemicals and the COD load of waste water. Lowering the Kappa number by one unit before bleaching can reduce the COD released in the bleach plant by approximately 2 kg COD/ADt. The lignin removed can be recovered and sent to the chemicals and energy recovery system (EU BREF pp p. 816).

## 2.4.2 Elemental chlorine bleaching process

24. Because of its potential of PCDD/F formation, elemental chlorine has been largely phased out throughout the world (e.g. in the EU, North and South America and others; Figure 3) as primary bleaching chemical in the last decades. This also reduce the risk of handling elemental chlorine (Evans, 2005; Kay, 2005).

25. Elemental chlorine ($Cl_2$) and hypochlorous acid (HClO) are electrophilic bleaching chemical agents that react with all unsaturated structures, namely lignin structures; with polysaccharide degradation products, such as hexenuronic acid (IUPAC name: (2S,3R,4S)-3,4-dihydroxy-2-[(2R,3R,4S,5R)-4-hydroxy-2,5-dimethoxyoxan-3-yl]oxy-3,4-dihydro-2H-pyran-6-carboxylic acid); and with extractive structures that contain carbon-carbon double bonds (Pulp Paper Mill 2015). These electrophilic bleaching agents are able to react with different unsubstituted aromatic carbon atoms in lignin to:

- Chlorinate (when the carbon is not bonded with an oxygen atom); or
- Chlorinate and depolymerize (via displacement of an α-hydroxyl group); or
- Merely depolymerize without chlorination (via hydroxylation).

26. These chlorination, or depolymerization reactions make lignin alkaline soluble, and it can be removed from pulp in the washing and alkaline extraction stages of the bleaching sequence (see Figure 4 below).

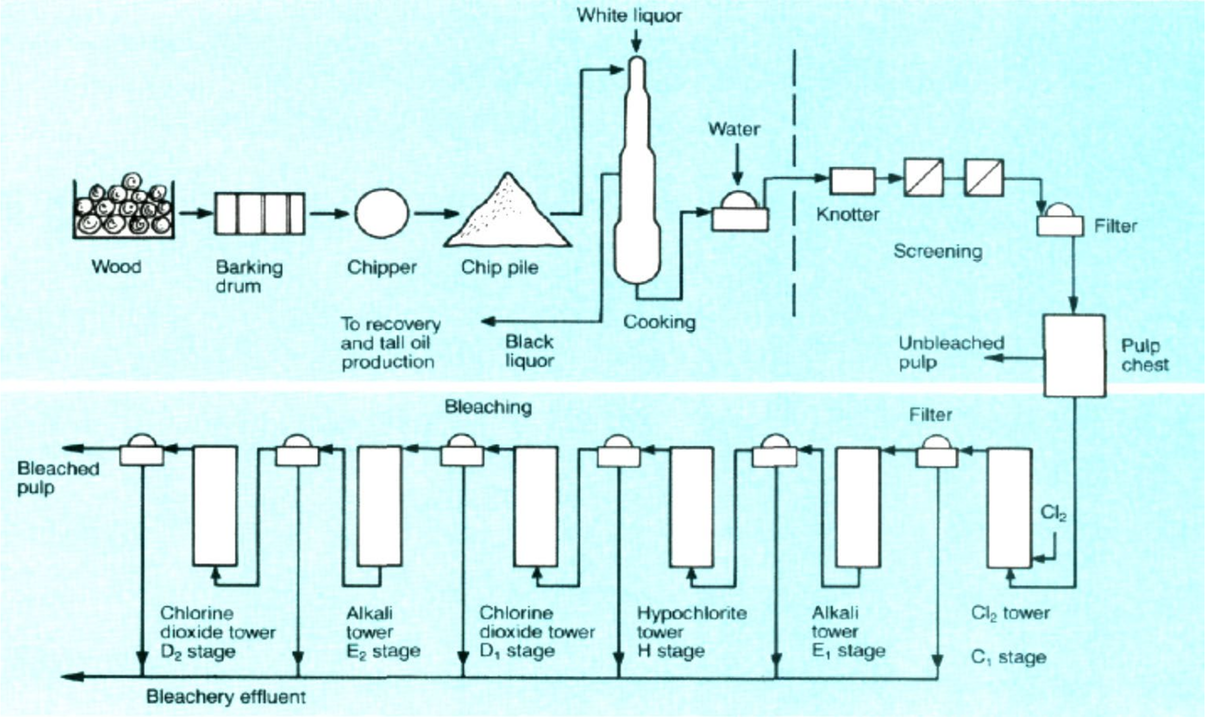

Figure 4: Scheme of a Kraft pulp mill, including a conventional bleach plant. (Source: Kringstad and Lindström, 1984)

27. Process steps for bleaching pulp with elemental chlorine may include the following (see also Table 1):

28. For example, CEH, CEHH, CHEH are used for lower brightness pulps; CEHEH, CCHEHH, CED, CEHD, CEHED are used for medium brightness pulp (up to 85 % GE brightness) and CEDED, CEHDED, CCHEDH, CDEODED, OCDEHD are used for high brightness (around 90 or 90 plus).

Hydrogen peroxide containing bleach stage produces high brightness pulps, for example, CEHDP and CEDPD produce above 90 plus percent GE brightness pulp (Pulp Paper Mill 2015).

29. The formation and emission of PCDD/PCDF in non-wood varied strikingly according to bleaching processes and raw materials. Elemental chlorine bleaching promoted the formation of tetra- to octachlorinated dibenzo-p-dioxins and 2,3,7,8-TCDF, while hypochlorite bleaching only gave rise to a significant increase of 2,3,7,8-TCDF. Bleaching with elemental chlorine and hypochlorite increased 2,3,7,8-TCDF 0.9−42.5 and 0.3−4.1 times, respectively. Most of the 2,3,7,8-TCDF formed at hypochlorite bleaching stage was partitioned into the effluent, which indicated that hypochlorite bleaching was also an important emission source of dioxins. The removal of PCDD/PCDF occurred during alkaline digestion, alkaline extraction, and hydrogen peroxide bleaching (Wang et al., 2012).

30. Chlorine dioxide is thermodynamically unstable and is usually manufactured at the place of use. In pulp mills, chlorine dioxide is produced from sodium chlorate ($NaClO_3$). For the reduction of chlorate, a number of reducing agents are commercially applied: methanol (extra safety measures required), hydrogen peroxide, sulphur dioxide and chloride ions. When chloride ions are used as reducing agent, elemental chlorine can be formed as a by-product and the $ClO_2$ water becomes saturated with chlorine, which is likeleylikely to form AOX (3.1.12.1 European Union *et al.*, 2015) and possibly PCDD/PCDF.

## 2.4.3 Elemental chlorine-free (ECF) bleaching process

31. A bleaching process using chlorine dioxide ($ClO_2$) or other chlorinated chemicals, but not elemental chlorine is referred to as ‘elemental chlorine-free’ (ECF). These chlorinated chemicals are electrophilic bleaching chemical agents that react with all unsaturated structures (see also Section 2.4.2).

32. 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 elemental 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, such as adsorbable organic halides (AOX) 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.

33. 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). For a typical flow diagram, see Figure 5 below.

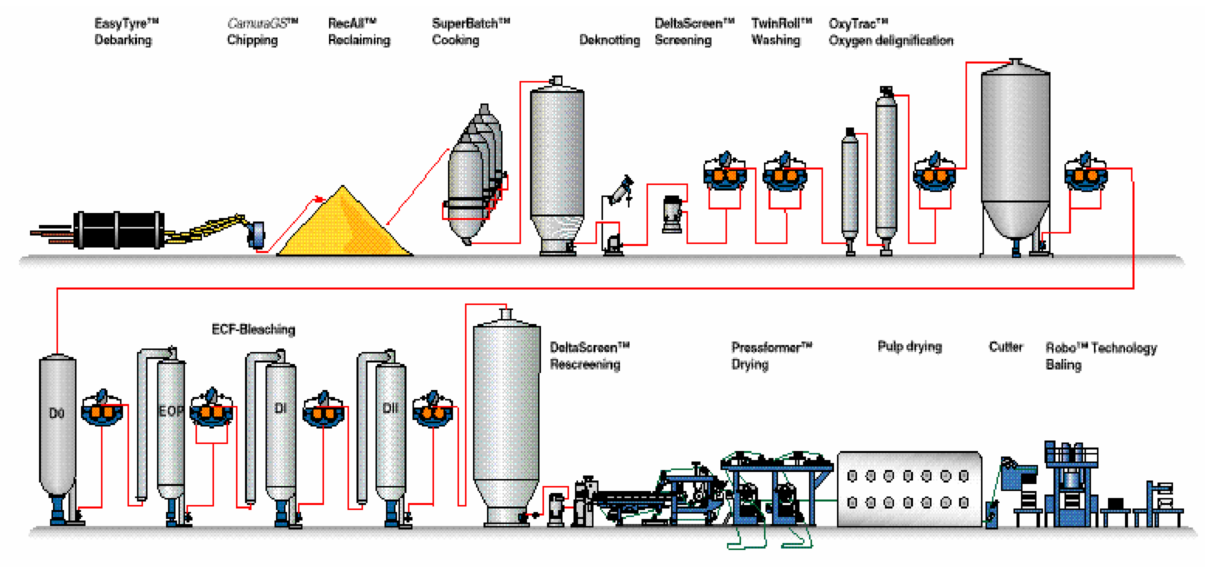

Figure 5: Typical flow diagram for modern Kraft pulping process with ECF bleaching; Source: Metso Automation Inc. (2007).

34. Modern elemental chlorine free (ECF) bleaching minimises the consumption of chlorine dioxide by one or a combination of the following bleaching stages: oxygen, hot acid hydrolysis stage, ozone stage at medium and high consistency, stages with atmospheric hydrogen peroxide and pressurised hydrogen peroxide or the use of a hot chlorine dioxide stage (European Union et al., 2015).

35. 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 may decrease the formation of molecular chlorine impurities and the unintentional formation of dioxins.

36. Elemental chlorine-free pulp (kraft pulp) bleached with $ClO_2$ holds the predominant position within the industry, accounting for more than three-quarters of the bleached pulp produced worldwide (Figure 3). Bleaching sequences used in ECF pulp mills in Europe are listed in Table 2 (European Union *et al.*, 2015). The alkaline (E) stages can be reinforced with oxygen or peroxide or both. The oxygen stage (O) is usually carried out in two stages, and is always carried out first since chemical recovery is possible. The D stage can be used instead of the Paa/Q stage.

Table 2: Example bleaching sequences of ECF (European Union *et al.*, 2015) (denominations, see Table 1)

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

37. According to Hostachy (2010), the use of limited ozone after the alkaline extraction stage in softwood pulping is an innovative solution to help mills optimizing pulp mill bleaching chemical costs.

38. However, PCDD/PCDF formation may still occur during ECF bleaching from $Cl_2$ that may be contained in $ClO_2$ or formed during the ECF bleaching process, in particular when using chloride as a reducing agent (European Union et al., 2015). The extent of such formation depends on the use of reducing agent, the amount of $Cl_2$ in the $ClO_2$ and on the quantity of lignin remaining in the pulp

(commonly expressed in “Kappa numbers”). With high Kappa numbers and more $Cl_2$ in the $ClO_2$, the probability of forming PCDD/PCDF increases (European Union *et al.*, 2015).

39. ECF bleaching is capable of reducing 2,3,7,8-TCDD and 2,3,7,8-TCDF to undetectable levels. However, the complete elimination of PCDD/PCDF in ECF-bleached effluents is a question of kappa number (related to the amount of lignin remaining in the pulp) and purity of $ClO_2$. With a high Kappa number and impure $ClO_2$ (*i.e.*, determined mainly by $Cl_2$ content) the probability of forming PCDD/PCDF increases. The ECF bleaching process is also capable of reducing the formation of the AOX compounds in the form of e.g. chlorophenols and chloroform and is able to reduce AOX formation by orders of magnitude (World Bank 2019). Complete prevention of AOX formation during the $ClO_2$ bleaching stage is not possible, due to the side reactions of HClO and $Cl_2$ in solution with residual lignin that undergo substitution reactions with the lignin molecules.

## 2.4.4 Totally chlorine-free (TCF) bleaching process

40. TCF bleaching is 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 (definition, see Glossary) 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.

41. Modern bleaching sequences for hardwood and softwood Kraft pulping are shown in Table 3.

42. No AOX is formed and released in the TCF bleaching process (Wennerström et al. 2002).

Table 3: Example bleaching sequences in a TCF bleaching process (denominations, see Table 1) (European Union *et al.*, 2015)

| TCF/Softwood | TCF/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) |
| Q/OP/(Q+Paa)/PO | O/OZPZP |
| O/O(Q)OP(Paa/Q)PO | OmPZPZP |

43. Ozone seems to have become the most common complements to peroxide in TCF bleaching sequences. The main purpose of using ozone is to provide more delignification power. Ozone activates the fibres towards hydrogen peroxide and these result in a greater brightness and a somewhat lower hydrogen peroxide consumption. On the other hand, the selectivity of ozone is poor. Excessive application, too high a temperature or application of other unsuitable treatments may lead to serious cellulose degradation. Ozone should preferably be applied under acidic conditions (pH ~2–3). Too high temperature (>70 °C) impairs the selectivity (European Union *et al.*, 2015).

## 2.4.5 Elimination mechanisms for PCDD/PCDF formation

44. Preventing the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF in the pulp bleaching process can be achieved by replacing the use of elemental chlorine with alternatives such as the ECF (Section

2.4.3) or TCF (Section 2.4.4) processes (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 and by increasing the active chlorine multiple (definition, see Glossary), as demonstrated in Figure 6. When the $ClO_2$ substitution level is higher than 85 %, 2,3,7,8-TCDD/TCDF is virtually eliminated (Figure 6).

For further reading, the report by SYKE (Tana and Lehtinen, 1996) and the review article on ”*The effect of the transition from elemental chlorine bleaching to chlorine dioxide bleaching in the pulp industry on the formation of PCDD/Fs*” (Axegard 2019) is recommended.

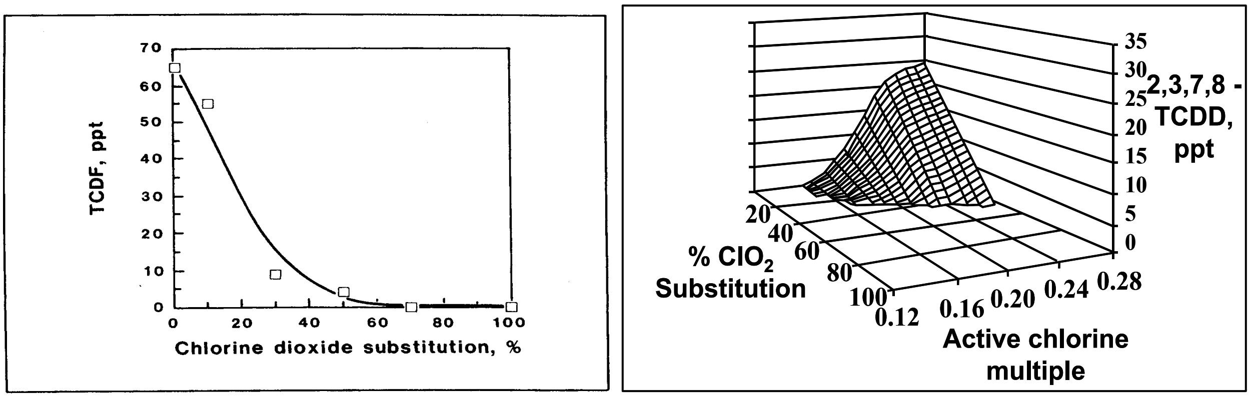

Figure 6: Left: Elimination of 2,3,7,8-TCDF with increasing substitution of chlorine dioxide for chlorine; Right: Effect of active chlorine multiple and chlorine dioxide substitution level on 2,3,7,8-TCDD formation (Berry *et al.*, 1991)

### 2.4.6 Non-wood bleaching process

45. Within a Global Environment Facility (GEF) project on “Dioxins Reduction from the Pulp and Paper Industry (P125528)” implemented by The World Bank, existing elemental chlorine-based bleaching process were replaced by elemental chlorine free (ECF) processes in non-wood pulp industries including the four different main types of non-wood fiber used in pulp production (bamboo, straw, reed and bagasse) (World Bank 2019). The substitution of elemental chlorine in the non-wood pulp industries is possible and by 2019, most non-wood pulp manufacturers in China had adopted the ECF or TCF bleaching technique, while a few were still using elemental chlorine bleaching (World Bank 2019) and since 2019 the use of elemental chlorine in pulp and paper production is prohibited in China (State Development and Reform Commission of China 2019).

46. Further some scientific publications have described PCDD/PCDF formation and reduction in non-wood bleaching process in industries (Wang *et al.*, 2012; Yang *et al.*, 2018) and in lab-scale experiments (Wang *et al.*, 2018; Xia *et al.*, 2020; Wang *et al.*, 2022).

47. Hot acid hydrolysis seems to have become common pretreatment methods for bleaching eucalyptus kraft pulps and for some hardwood pulps such as birch. The process is used to remove hexenuronic acids formed during the pulping process (Hart, 2019).

### 2.4.7 Enzyme-aided bleaching process

48. Enzyme treatment before bleaching has been in use at some plants in North America since 1991. It can be combined with different bleaching sequences to enhance the effectiveness of the chemicals used but typically results in a small loss of yield (European Union et al. 2015). Enzymes, such as xylanase, might offer benefits in the pulp and paper industry by reducing energy demand (European Union et al. 2015). For non-wood bleaching process, the measured PCDD/PCDF concentrations (as TEQ) in solid samples in an elemental chlorine bleaching process were higher in

the enzyme added process than in the conventional process but in the effluents, the samples from the enzyme-aided process had lower values than in the conventional process (Fang et al. 2017).

# 3 BEST AVAILABLE TECHNIQUES FOR PRODUCTION OF BLEACHED PULP WHEN USING ELEMENTAL CHLORINE OR CHEMICALS GENERATING ELEMENTAL CHLORINE FOR BLEACHING

49. The use of elemental chlorine in the pulp and paper industry cannot be considered BAT/BEP (e.g. see European Union, 2014, BAT 19 or State Development and Reform Commission of China 2019) but it is still used in some pulp and paper industries e.g. in India and possibly some other countries.

50. The principal best available techniques for minimizing or eliminating the formation of 2,3,7,8-TCDD/TCDF in wood and non-wood pulp bleaching processes are as follows (Berry *et al.*, 1991):

- For new and existing sources: use of ClO2 (elemental chlorine-free bleaching) or chlorine-free chemicals for bleaching.
- For existing sources that currently use elemental chlorine: elimination/phase-out of elemental chlorine by replacing it with ClO2 (elemental chlorine-free bleaching) or with chlorine-free chemicals.

  During this phase-out process the following measures are to be applied:
  - reduction of the application of elemental chlorine by decreasing the multiple or increasing the substitution of ClO2 for elemental chlorine;
  - effective brownstock washing to enable the reduction of chlorine multiple.
- Utilization of dibenzo-p-dioxin (DBD)-free and dibenzofuran (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 et al., 1997).

51. Further BAT of the European Union for pulp and paper mills is described in Chapter 5 (Annex ) below.

52. The Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs under Article 5 of the Stockholm Convention lists classes to describe the PCDD/PCDF releases from pulp and paper mills as follows (UNEP, 2013):

**“Class 1** facilities use the Kraft process for pulping non-wood fibres that are potentially contaminated with pentachlorophenol (PCP) and bleach with $Cl_2$.

**Class 2** facilities use the Kraft process for pulping fibres that are PCP-free and bleach with $Cl_2$.

**Class 3** facilities use the Kraft process for pulping and bleach first with $Cl_2$, followed by non-chlorine bleaching technologies.

**Class 4** facilities use the sulfite process for pulping and bleach with $Cl_2$.

**Class 5** facilities use the Kraft process for pulping and bleach with chlorine dioxide ($ClO_2$).

**Class 6** facilities use the sulfite process for pulping and bleach with $ClO_2$ or with totally chlorine-free (TCF) technologies.

**Class 7** facilities use thermo-chemical processes (TMP) to produce pulp and bleach via lignin-saving methods that use sodium dithionite ($Na_2S_2O_3$; hydrosulfite), peroxide ($H_2O_2$) or both sequentially requiring some heating (Isoaho 2019).

**Class 8** facilities are those engaged in recycling paper from contaminated waste paper – paper that is made from pulp produced by Class 1 through Class 4 facilities.

**Class 9** facilities are those engaged in recycling paper from modern paper – paper derived from pulp produced by Class 5 and Class 7 facilities."

# 4 ACHIEVABLE PERFORMANCE LEVELS ASSOCIATED WITH BEST AVAILABLE TECHNIQUES AND BEST ENVIRONMENTAL PRACTICES

## 4.1 BAT performance levels in bleached pulp production

53. In the European Union, elemental chlorine ($Cl_2$) and hypochlorite (NaOCl) have been phased out as primary bleaching chemicals (Figure 3) following PARCOM "Decision on the Phasing-out of the Use of Molecular Chlorine ($Cl_2$) in the Bleaching of Kraft and Sulfite Pulp" (PARCOM, 1996).

54. According to the European Union BAT Reference Document (BREF) for pulp and paper (European Union *et al.*, 2015), no emission monitoring for PCDD/PCDF took place. Sampling points or production process steps included recovery boiler, lime kiln, burners for odorous gases, weak gases, auxiliary or bark burners/fluidized bed combustion, and rejects/sludge co-incineration (Table 2.5 in European Union *et al.*, 2015)

55. Achieved environmental benefits (page 263, European Union *et al.*, 2015): "ECF bleaching is capable of reducing 2,3,7,8-TCDD and 2,3,7,8-TCDF to undetectable levels, because of the substitution of bleaching with elementary chlorine by modern ECT or TCF bleaching. However, the complete elimination of PCDD/PCDF in ECF-bleached effluents is a question of Kappa number and purity of $ClO_2$. With a high Kappa number and impure $ClO_2$ (i.e., high concentration of $Cl_2$) the probability of forming PCDD/PCDF increases. Modern ECF bleaching also prevents formation or reduces other pollutants, including AOX". The bleaching with TCF can minimize and eliminate the release of AOX. A reduction of AOX was achieved by a combination of several measures: in western Europe, the use of elemental chlorine has been completely replaced by $ClO_2$ use and the use of chlorine free bleaching chemicals such as molecular oxygen, hydrogen peroxide, ozone or peracetic acid (p.30, European Union *et al.*, 2015)).

56. The removal of PCDD/PCDF from flue-gas can be achieved with activated carbon or coke. Generally achievable values are <0.1 ng I-TEQ/Nm$^3$. Lower values are possible, depending on the dosage of adsorption material, e.g., activated carbon (p 648, European Union *et al.*, 2015).

57. Within a Global Environment Facility (GEF) project on "Dioxins Reduction from the Pulp and Paper Industry" (P125528) implemented by The World Bank, elemental chlorine has been substituted in non-wood pulp industries including bamboo, straw and reed pulp mills (World Bank, 2019). Table 4 and Table 5 summarize findings from a World Bank project for three paper mills in China that substituted elemental chlorine bleaching with ECF bleaching for non-wood pulp (World Bank, 2019). The reduction rates measured as PCDD/PCDF per Unit Pulp (ng/ADt) were 77% and 98%. For a bagasse pulp mill the reduction rate measured as dioxins per Unit Pulp (ng/ADt) was 88% (World Bank, 2019).

Table 4: Dioxins release reduction in non-wood pulp mills in China by substitution of elemental chlorine bleaching by ECF (World Bank, 2019 p. 78/79)

| Mill | | Baseline (CEH) | BAT/BEP (ECF) | Reduction Rate |
|---|---|---|---|---|

| | Capacity (ADt) | Dioxins per Unit Pulp (ng/ADt) | Dioxins Per Year (mg) | Dioxins Per Unit Pulp (ng/ADt) | Dioxins Per Year (mg) | After BAT/BEP (ECF) Implementation |
|---|---|---|---|---|---|---|
| Sichuan Jinfu (bamboo pulp) | 52,000 | 1,498.60 | 78 | 28.49 | 1 | 98 |
| Henan Baiyun (straw pulp) | 37,000 | 1,808.40 | 67 | 412.63 | 15 | 77 |
| Hunan Linyuan (reed pulp) | 51,000 | 2,206.25 | 113 | 33.98 | 2 | 98 |

*Note*: ADt: Air dry ton—industry standard for pulp weight, 10 percent moisture: **(ng/ADt)**.
CEH: C: chlorine ($Cl_2$), E: alkaline extraction, H: hypochlorite (OCl)

Table 5: Dioxins release reduction in a bagasse-based mill in China by substitution of elemental chlorine bleaching by ECF (World Bank 2019 p. 78/79)

| Mill | Capacity (ADt) | Baseline (CEH) | | BAT/BEP (ECF) | | Reduction Rate After BAT/BEP (ECF) Implementation |
|---|---|---|---|---|---|---|
| | | Dioxins Per Unit Pulp (ng/ADt) | Dioxins Per Year (mg) | Dioxins Per Unit Pulp (ng/ADt) | Dioxins Per Year (mg) | |
| Guangxi Nanhua (bagasse pulp) | 98,000 | 1,212.78 | 119 | 142.56 | 14 | 88% |

No data from other countries or regions were made available.

## 4.2 BAT measures at air pollution control devices and performance levels

58. Depending on fuels utilized, design and operation of combustion plants within a pulp mill, injection of adsorbents like activated carbon (also applicable for the reduction of mercury), rapid quenching using wet scrubbing/flue-gas condenser or selective catalytic reduction (SCR) are BAT for reducing organic compounds such as PCDD/PCDF. (European Union, 2021)

59. Sludge burners typically burning primary solids like waste fibres and biological solids (from wastewater treatment) did not show increased PCDD/PCDF emissions when rejects were co-incinerated (p. 159, European Union *et al.*, 2015). Measurements at two German plants from incineration of rejects and sludge were below 0.1 ng TEQ/Nm³ @11 % $O_2$ (European Union *et al.*, 2015 Table 6.17 p. 593).

## 4.3 Performance reporting

60. 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 Part II, chapter 7a of the 'Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs' (UNEP, 2013).

61. Note: 17th BImSchV, Germany, applies $WHO_{2005}$-TEFs and includes 17 PCDD/PCDF and 12 dl-PCB; the 2015 BREF refers to I-TEFs, which include only 17 PCDD/PCDF in the TEQ. The respective EU directive on industrial emissions (integrated pollution prevention and control) refers to I-TEFs and includes only 17 PCDD/PCDF (European Union, 2010).

# 5 ANNEX: RELEVANT INFORMATION FROM EU REGULATION "IMPLEMENTATION OF BAT FOR THE PRODUCTION OF PULP AND PAPER" (EUROPEAN UNION 2014)

62. For the European pulp and paper industry the only relevant BAT to prevent the formation of PCDD/PCDF is BAT 19[1] (European Union, 2014), which states: "In order to reduce emissions of pollutants into receiving waters from the whole mill, BAT is to use TCF or modern ECF bleaching (see below), and a suitable combination of the techniques specified in BAT 13, BAT 14, BAT 15 and BAT 16 and of the techniques given below (European Union, 2014).

- TCF - Totally chlorine-free bleaching: In TCF bleaching, the use of chlorine containing bleaching chemicals is completely avoided and thus so are the emissions of organic and organochlorinated substances from bleaching.
- Modern elemental chlorine-free (ECF) bleaching: Modern ECF bleaching minimises the consumption of chlorine dioxide by using one or a combination of the following bleaching stages: oxygen, hot acid hydrolysis (Ahot) stage, ozone stages (Z) at medium and high consistency, stages with atmospheric hydrogen peroxide (P) and pressurised hydrogen peroxide (PO) or the use of a hot chlorine dioxide stage (Dhot).

63. BAT-associated emission level for the direct waste water discharge to receiving waters from a bleached Kraft pulp mill for AOX is 0-0.2 kg/Adt yearly average using the average of at least 6 AOX measurements in waste water per year. (European Union et al. 2015; p.792)

64. For member states of the European Union, BAT conclusions also address broader issues than PCDD/PCDF emissions (European Union, 2014). The following highlights dioxin-related measures:

65. The European Union defines BAT conclusions for integrated Kraft pulp and paper mills as follows (European Union 2014):

Section 1.2.1. Waste water and emissions to water - BAT 19[1].

a) Modified cooking before bleaching.
b) Oxygen delignification before bleaching.
c) Closed brown stock screening and efficient brown stock washing.
d) Partial process water recycling in the bleach plant.
e) Effective spill monitoring and containment with a suitable recovery system.
f) Maintaining sufficient black liquor evaporation and recovery boiler capacity to cope with peak loads.
g) Stripping the contaminated (foul) condensates and reusing the condensates in the process.

66. The European Union defines BAT conclusions for the sulfite pulping process as follows:

**Waste water and emissions to water:** BAT 33 [1]. In order to prevent and reduce emissions of pollutants into receiving waters from the whole mill, BAT is to use a suitable combination of the techniques specified in BAT 13, BAT 14, BAT 15 and BAT 16 and of the techniques given below (European Union 2014).

a) Extended modified cooking before bleaching.
b) Oxygen delignification before bleaching.
c) Closed brown stock screening and efficient brown stock washing.

---

[1] In the European BAT Conclusions the individual conclusions are numbered consecutively.

d) Evaporation of effluents from the hot alkaline extraction stage and incineration of concentrates in a soda boiler.

e) TCF bleaching.

f) Closed-loop bleaching.

g) MgO-based pre-bleaching and recirculation of washing liquids from pre-bleaching to brown stock washing.

h) pH adjustment of weak liquor before/inside the evaporation plant.

i) Anaerobic treatment of the condensates from the evaporators.

j) Stripping and recovery of $SO_2$ from the condensates of evaporators.

k) Effective spill monitoring and containment, also with chemical and energy recovery system.

Emissions to air: Note: sulfite pulp mills using calcium-based cooking do not operate a recovery boiler.

**BAT conclusions for mechanical pulping and chemical/mechanical pulping:** The BAT conclusions in this section apply to all integrated mechanical pulp, paper and board mills and to mechanical pulp mills, CTMP and CMP pulp mills. **BAT 49, BAT 51, BAT 52c and BAT 53**[1] also apply to papermaking in integrated mechanical pulp, paper and board mills, in addition to the BAT conclusions in this section.

**Section 1.4.1. Waste water and emissions to water.**

67. BAT 40[1]. In order to reduce fresh water use, waste water flow, and the pollution load, BAT is to use a suitable combination of the techniques specified in BAT 13, BAT 14, BAT 15 and BAT 16[1] and of the techniques given below (European Union 2014).

a) Counter-current flow of process water and separation of water systems.

b) High consistency bleaching.

c) Washing stage before the refining of softwood mechanical pulp using chip pre-treatment.

d) Substitution of NaOH by $Ca(OH)_2$ or $Mg(OH)_2$ as alkali in peroxide bleaching.

e) Fibre and filler recovery and treatment of white water (papermaking).

f) Optimum design and construction of tanks and chests (papermaking).

68. Chlorine dioxide and ozone have to be produced on site (see Section 3.1.12 (European Union *et al.*, 2015)).

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