

ENVIRONMENTAL FOOTPRINT COMPARISON TOOL

A tool for understanding environmental decisions related to the pulp and paper industry



EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON DISCHARGE TO WATER

Organochlorine Compounds in Wastewater

The generation and release of certain water pollutants from chemical pulp bleaching operations are affected by the choice of bleaching chemicals, and the industry's shift from chlorine bleaching to ECF bleaching has altered wastewater characteristics.

Chlorinated organic by-products of chemical pulp bleaching that are the most toxic and recalcitrant to wastewater treatment are chlorinated dioxins and furans and highly chlorinated phenolic compounds. These compounds can be produced during elemental chlorine bleaching of chemical pulps, but their presence at measurable levels is virtually eliminated in ECF bleaching.

The reduction in chlorinated organic by-products from use of chlorine dioxide occurs because, as the chlorine dioxide substitution level increases, the amount of chlorine available to react with lignin and other organic compounds decreases. Moreover, elemental chlorine and chlorine dioxide differ fundamentally in the way they chemically react with lignin in unbleached pulp. Compared to elemental chlorine bleaching, AOX, a measure of total chlorinated organic material, is reduced by 90% or more with ECF bleaching. Greatest reductions in chlorinated substances accompany practices that reduce the quantities of lignin in pulps prior to ECF bleaching sequences. TCF bleaching would eliminate the generation of chlorinated compounds in the bleach plant.

Chloroform, a by-product formed when pulp is bleached with sodium hypochlorite or chlorine, is generated in much smaller quantities when chlorine dioxide is used in place of the former chemicals. Emission reductions for chloroform of greater than 99% have resulted from the application of ECF bleaching and elimination of chlorine and hypochlorite from the bleaching sequence.

Mechanical pulp bleaching and recovered fiber brightening systems typically use chemicals such as hydrogen peroxide, sodium hydrosulfite or, for recycled pulps, formamidine sulfinic acid (FAS) or sodium hypochlorite. Of these, hypochlorite is the only chemical that contains chlorine. The use of peroxide, hydrosulfite, or FAS in place of hypochlorite for recovered fiber brightening would eliminate the production of chlorinated organic compounds.

Bleaching of (Virgin) Chemical Pulps

The characteristics of wastewater from a bleached chemical pulp mill are highly influenced by bleaching operations because a large portion of the wastewater produced at a mill originates from bleaching operations. Compounds that derive from bleaching operations and that are known to be affected by the use of the various bleaching chemicals include dioxin (2,3,7,8-TCDD) and furan (2,3,7,8-TCDF), substituted chlorinated phenolic compounds, chloroform, and adsorbable organic halides, or AOX (a measure of total chlorinated organic material).

Dioxin and furan were shown to be unintended byproducts of chemical pulp bleaching with chlorine in the 1980s. With respect to pulp bleaching, the specific compounds produced were limited to 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and tetrachlorodibenzofuran (2,3,7,8-TCDF). Extensive measurement of effluents from ECF bleach plants shows that measurable levels of 2,3,7,8-TCDD are not found and that 2,3,7,8-TCDF is only very rarely found at quantifiable levels (USEPA 2006). TCF bleaching eliminates any possibility that these compounds might be formed at levels below analytical detection limits.

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Chlorinated phenolic compounds of concern with respect to toxicity and resistance to biological treatment include the highly substituted phenolics. These include the tri-, tetra-, and penta-substituted phenols, catechols, and guaiacols. Of these, 13 compounds are predominant, and some were shown to be generated during the chlorine bleaching of chemical pulps. Extensive measurement of effluents from ECF bleach plants shows that these compounds are only very rarely detected at quantifiable levels (EPA 2006). TCF bleaching eliminates any possibility that these compounds might be formed at levels below analytical detection limits.

Chloroform is a by-product of bleaching with sodium hypochlorite, chlorine, and to a much lesser extent, chlorine dioxide. Chloroform is not known to be produced by oxygen, peroxide, or other non-chlorinated bleaching chemicals. Figure C19 shows the magnitude of chloroform generation associated with a typical bleach line using chlorine and hypochlorite and a typical line using only chlorine dioxide (ECF). Chloroform loads from TCF mills would be zero.

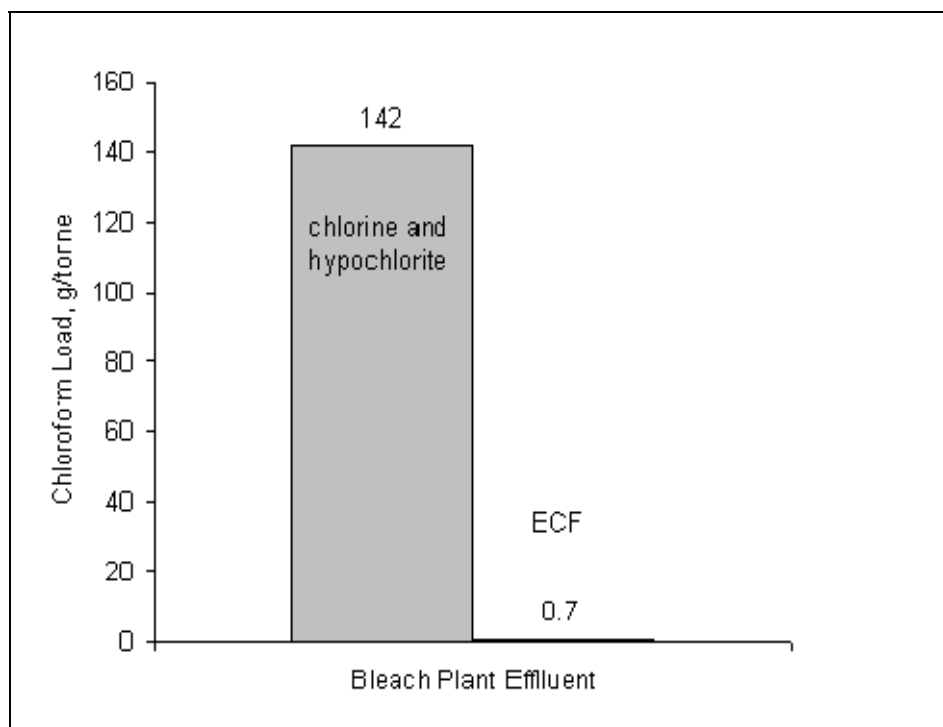


Figure C19. Chloroform Load from Chlorine + Hypochlorite and Chlorine Dioxide (ECF) Bleaching of Kraft Pulp (Source: USEPA 1997)

As is apparent in the figure, 99.5% of the reduction in chloroform emissions is achieved through implementation of ECF bleaching. The remaining 0.5% reduction could be achieved through TCF bleaching.

AOX is a measurement parameter representing the amount of chlorinated organic material present in wastewater. The chemistry of bleaching with chlorine is such that a portion of the chlorine attaches to organic structures in wood, resulting in chlorinated organic compounds. The chemistry of chlorine dioxide in bleaching is quite different from that of chlorine, resulting in much lower levels of chlorinated organic material and thus much lower AOX. TCF bleaching does not produce AOX.

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For both chlorine and chlorine dioxide bleaching, the amount of AOX formed is related to the charge (addition rate) of chlorine or chlorine dioxide in the early bleaching stages. Hardwood pulps require lower chemical charges to achieve a given brightness relative to softwood pulp and thus produce less AOX. Similarly, the use of oxygen delignification and/or extended cooking prior to pulp bleaching of hardwood or softwood reduces the need for chemicals in the subsequent bleaching stages and thus reduces the amount of AOX generated.

AOX is partially treatable in biological wastewater treatment systems yielding effluent loads that are 50 to 70% lower than bleach plant loads. Some of the removal takes place within the mill due to chemical reactions when waste streams are mixed.

Figure C20 shows the estimated loads of AOX in biologically treated effluents at mills using various bleaching sequences.

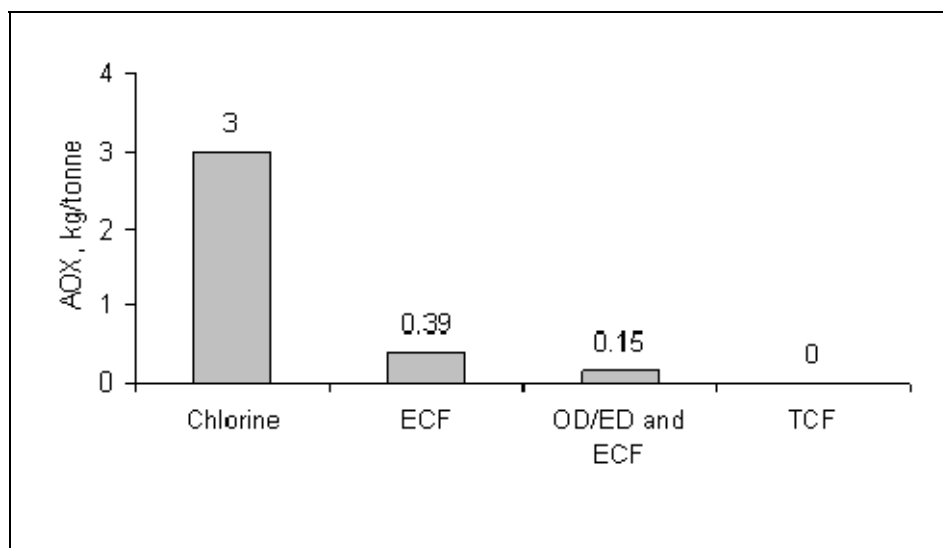


Figure C20. AOX Loads in Treated Effluents from Softwood Bleaching Sequences
(Source: USEPA 1997)

Bleaching of Mechanical and Chemi-Mechanical Pulps

Mechanical and chemi-mechanical pulps are typically bleached (brightened) using sodium peroxide and/or sodium hydrosulfite or other non-chlorine containing chemicals (Dence and Reeve 1996). Thus, bleaching of these pulps does not produce chlorinated by-products.

Brightening of Recovered Fiber

Brightening of most recycled pulps is accomplished with either sodium hypochlorite or non-chlorine based chemicals such as hydrogen peroxide, sodium hydrosulfite, or formamidine sulfinic acid (FAS) (Dence and Reeve 1996). Mills that do not use hypochlorite or other chlorine-containing chemicals for brightening are said to operate process chlorine free, or PCF.

Chloroform is produced as a by-product of brightening with sodium hypochlorite. The generation of chloroform in recovered fiber brightening stages using hypochlorite is similar in magnitude to that associated with hypochlorite bleaching of virgin pulps; ranging between about 0.12 and 1.2 kg/air dry metric ton (ADMT) of pulp (Dence and Reeve 1996). A portion of this chloroform would be emitted in

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bleach plant vents and the remainder with bleach plant wastewater sent for treatment. Elimination of hypochlorite from the brightening system in favor of peroxide or other non-chlorine containing brightening agents would eliminate most or all generation of chloroform.

Dioxins and highly chlorinated phenolics are not commonly measured at recovered fiber operations. The chemistry of formation of these compounds in kraft pulp bleaching provides little reason to expect that these compounds are formed in hypochlorite bleaching (NCASI 2001). Measurements of treated effluents for dioxins and furans at mills in the 1990s showed 2,3,7,8-TCDD to be below analytical minimum levels in all cases and 2,3,7,8-TCDF to occur only very rarely and this was likely due to the presence of the compound in the recovered paper supply (NCASI 1994). Conversion to process chlorine free (PCF) brightening processes may provide some assurance that dioxins and highly chlorinated phenolics are not discharged, but given the low or non-detectable levels in treated effluents, it is not possible to quantify the reduction that might be achieved.

AOX can be formed in sodium hypochlorite brightening of recovered fiber. Loads from recovered fiber brightening systems or treated final effluents from such mills, however, have not been widely measured and reported. Use of PCF brightening would not lead to AOX generation and thus, conversion from hypochlorite bleaching would be expected to result in a reduction of AOX discharged with treated effluents.

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