CHLORINATED COMPOUNDS

EFFECTS OF RECYCLED FIBER USE ON CHLORINATED COMPOUNDS

Pulp Bleaching and Brightening

Until the 1990s, most chemical pulp mills used chlorine and chlorine dioxide to bleach pulp and some mills also used sodium hypochlorite. The discovery, in the mid-1980s, that dioxin can be formed when chlorine is used to bleach chemical pulps led to changes in the chemicals used for pulp bleaching. The most notable change was the elimination of chlorine and hypochlorite in favor of chlorine dioxide in the sequence referred to as “elemental chlorine free” (ECF) bleaching. This conversion also led to the increased use of oxygen and hydrogen peroxide in the pulping and/or bleaching sequence. Complete elimination of all chlorine compounds in pulp bleaching in favor of oxygen, peroxide and other non-chlorine containing chemicals is termed “totally chlorine free” (TCF) bleaching.

The characteristics of wastewater from a bleached chemical pulp mill are highly influenced by bleaching operations. This is because a large portion of the wastewater produced at a mill originates from bleaching operations given that its chemical characteristics do not allow it to be recycled in a straightforward manner, compared to effluents from other areas of the mill. Compounds that derive from bleaching operations, the generation of which is known to be affected by the use of the various bleaching chemicals, include dioxin and furan (2,3,7,8-TCDD and 2,3,7,8-TCDF), substituted chlorinated phenolic compounds, chloroform, and adsorbable organic halides (AOX; a measure of total chlorinated organic material).

2,3,7,8-TCDD and 2,3,7,8-TCDF

In the 1980s, 2,3,7,8-TCDD and 2,3,7,8-TCDF (sometimes called “dioxin” and “furan”, respectively) were found to be unintended byproducts when chlorine was used for virgin chemical pulp bleaching. 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). In virgin chemical pulp bleaching, TCF bleaching eliminates any possibility that these compounds might be formed, even at levels below analytical detection limits.

Recycled mills do not use chlorine for bleaching but some recycling mills that produce tissue or fine paper use sodium hypochlorite for brightening of pulp. Hypochlorite is not used in brightening newsprint. The chemistry of formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF in kraft pulp bleaching, described in NCASI Technical Bulletin No. 819 (NCASI 2001) provides little reason to expect that these compounds are formed in hypochlorite bleaching at virgin or recycled mills. Measurements of treated effluents from recycled mills for dioxins and furans (NCASI 1994) 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 – likely due to the presence of the compound in the recovered paper supply rather than pulp brightening.

Chlorinated Phenolic Compounds

A number of chlorinated phenolic compounds are of concern because of their toxicity and resistance to biological treatment. Of particular concern are the highly substituted phenolics, i.e., 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 (USEPA 2006). TCF bleaching eliminates any possibility that these compounds might be formed, even at levels below analytical detection limits.

While as noted above, some recycling mills use sodium hypochlorite for brightening of pulp, the chemistry of formation of highly substituted phenolics in kraft pulp bleaching, described in NCASI Technical Bulletin No. 819 (NCASI 2001), provides little reason to expect that chlorinated phenolic compounds are formed in hypochlorite bleaching in virgin or recycled mills.

Chloroform

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 R6 shows the magnitude of chloroform generation associated with a typical virgin pulp bleach line using chlorine and hypochlorite and a typical line using only chlorine dioxide (ECF). Chloroform loads from TCF mills would be zero.

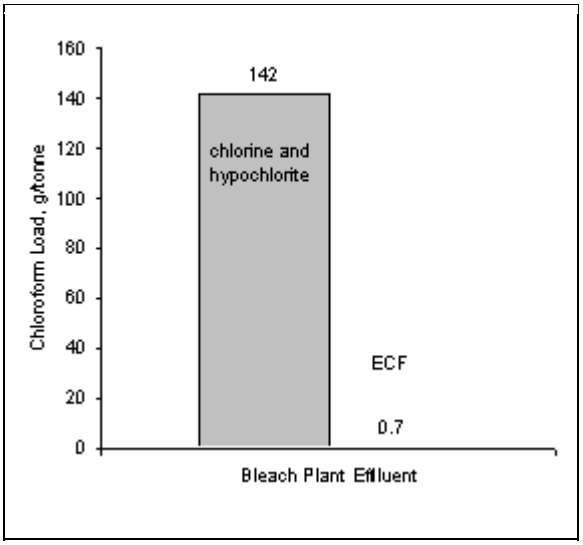

Figure R6.
Chloroform Load from Chlorine+Hypochlorite and Chlorine Dioxide (ECF) Bleaching of Kraft Pulp (USEPA 1997)

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

Chloroform is also produced as a by-product of brightening recovered fiber 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 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.

AOX

AOX is a non-specific measurement parameter representing the amount of chlorinated organic material present in wastewater. It is often used as a general indicator of the amount of chlorine and chlorine-compounds used in virgin pulp bleaching. It is seldom measured at recycling mills, however.

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