

An Assessment of the Formation of 2378-TCDD and 2378-TCDF when Chlorine Dioxide is the Oxidizing Agent in the First Stage of Bleaching of Chemical Pulp

Prepared for the Alliance for Environmental Technology
by a Scientific Advisory Panel

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1. EXECUTIVE SUMMARY

This review was conducted at the request of the Alliance for Environmental Technology by a Science Advisory Panel specifically convened for this purpose. The task put to the Panel was to prepare an independent expert opinion and assessment of the formation of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2378-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2378-TOOF) when chlorine dioxide (ClO_2) completely replaces chlorine (Cl_2) in the first stage of chemical pulp bleaching.

In preparing this review, the Panel examined over 150 relevant technical papers, studies and compilations of analytical data. The opinion was developed by examining the chemistry of formation of 2378-TCDD and 2378-TCDF in chemical pulp bleaching, the chemistry of chlorine dioxide bleaching, mill data and ecosystem studies. The Panel notes that the conclusions of this assessment were derived predominantly from information available for the kraft process. It was not possible to derive conclusions for the sulfite process owing to a scarcity of available information.

The major issues and conclusions of this assessment were:

1. Ohemical pulp bleaching with chlorine (Cl_2) may produce polychlorinated dioxins and furans of which the three congeners 2378-TCDD, 2378-TCDF and 1 278-TCDF will be found in the highest concentrations, with the two T_4CDF isomers appearing in approximately 1:1 ratio.
2. The main mechanism of 2378-TCDD/F formation is via electrophilic aromatic substitution of precursor molecules dibenzo-p-dioxin (DBD) and dibenzofuran (DBF) by chlorine. These precursors may be present in wood, but may also be introduced into the unbleached pulp from extraneous sources such as defoamers.
3. When bleaching with Cl_2 , the most effective method for minimizing the formation of 2378-TCDD and 2378-TCDF is by lowering the ratio of applied Cl_2 to residual lignin in unbleached pulp, or the chlorine multiple. Replacement of Cl_2 with chlorine dioxide in the first stage of pulp bleaching is an effective way to achieve this reduction.
4. Chlorine dioxide (ClO_2) and Cl_2 react with lignin by different chemical mechanisms. Chlorine dioxide itself does not directly produce organochlorine compounds, but chlorinated organic compounds are nevertheless produced, albeit in lower amounts when ClO_2 completely replaces Cl_2 . Their formation is via electrophilic substitution reactions of oxidizable organic components with hypochlorous acid (HOCl), one of the most important intermediates of ClO_2 reactions with residual lignin. The preferred reactions of HOCl with residual lignin are oxidative, and the extent to which it participates in electrophilic substitution reactions is significantly smaller than that of chlorine.
5. The examination of analytical results for laboratory and mill bleaching, the latter comprising 163 samples from 9 Canadian, 6 U.S. and two Swedish mills where ClO_2 had completely replaced Cl_2 in the first stage of bleaching, showed that 2378-TCDD was not found in either mill effluents at detection limits ranging from 0.3-9 pg/L (ppq), or in bleached pulp at detection limits of 0.1-0.3 pg/g (ppt). Therefore, complete replacement of Cl_2 with ClO_2 in the first stage of bleaching results in virtual elimination of 2378-TCDD. *A chemical compound is virtually eliminated when it cannot be detected in 100% of the samples analyzed using the best detection techniques available at the time.*
6. At 6 of the 17 mills mentioned above, 2378-TCDF was not detected in either mill effluents or in bleached pulp. At 5 of these mills, 2378-TCDF was seldom detected, while at 6 of the mills, 2378-TCDF was detected frequently. At the mills where 2378-TCDF was detected, the most probable cause was elevated amounts of dibenzofuran (DBF) precursor in the unbleached pulp. However, in a few cases sources external to the bleaching process could not be ruled out.
7. A hypothetical model was developed to explain the non-detection of 2378-TCDD and occasional detection of 2378-TCDF found from the review of lab and mill analytical data for ECF bleaching. It was hypothesized that the formation of 2378-TCDD and 2378-TCDF when ClO_2 has completely replaced Cl_2 may occur via a series of consecutive electrophilic substitution reactions of HOCl and its equilibrium product Cl_2 with DBD and DBF. The model assumed that the effective amount of HOCl and Cl_2 available for chlorination reactions during bleaching with ClO_2 could be approximated by the total atomic chlorine in the ClO_2 charged. While more data are needed to verify the new model, its predictions fit the experimental results (below).
8. The model suggests that the formation of 2378-TCDD and 2378-TCDF decreases exponentially and in a continuous fashion with increasing replacement of Cl_2 with ClO_2 . This implies that theoretically there is no critical chlorine multiple below which the formation of 2378-TCDD and 2378-TCDF is completely inhibited.

However, the model also predicts that for ECF bleaching, the concentration of 2378-TCDD will be less than the present lowest detection limit and that 2378-TCDF will be at non-detectable levels as long as the concentration of the precursor DOF is less than about 10 ppb (ng/g). Therefore, in agreement with the analytical data, the model predicts that complete replacement of Cl_2 by ClO_2 results in a virtual elimination of 2378-TCDD and a dramatic reduction in the concentration of 2378-TCDF.

9. Downstream of mills which have completely replaced Cl_2 with ClO_2 , concentrations of 2378-TCDD and 2378-TCDF in fish were found to be declining rapidly. More importantly, in the only case known to the Panel of a new bleached kraft pulp mill which has never used Cl_2 and only used ClO_2 for bleaching, after one year of operation, 2378-TCDD and 2378-TCDF were not detected (at 0.1 ppt) in fish caught directly downstream of the mill.
10. Taken together, the available data, although limited with regard to specific ecological responses, support the conclusion that at bleached chemical mills, where ClO_2 has completely replaced Cl_2 , no adverse effects caused by 2378-TCDD or 2378-TCDF from bleaching should be expected from mill effluents.