DIOXIN IN PULP & PAPER

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INTRODUCTION

Four main sources for dioxins have been identified and intensively discussed:

1) Manufacture and application of Cl-organic pesticides and PCBs;
2) Combustion processes, esp. municipal waste incineration, but also automobile exhaust, copper smelters, residential burning;
3) Pulp and paper industry;
4) Manufacture, accidental fires and discharge of brominated flame retardants.

Amongst the above sources the subject "pulp & paper" and "dioxin" is a relatively recent one but very evident. Within the last few years much public discussion and concern has arisen. This development is reflected by the increasing number of publications. Table 1 shows the number of publications listed in the File CA of the Chemical Abstract Service (CAS, Columbus, Ohio) dated on August 30, 1990 that matches both PCDD/PCDF (in several variations) and pulp or paper listed:

Table 1: Numbers of Publications on Dioxins AND Pulp and/or Paper Listed by CAS (Update: 08/30/1990)

Year	Number
Before 1987	0
1987	2
1988	5
1989	35
1990	2
DIOXIN'89	33
DIOXIN'90	23

It should be noted that papers presented at the annual Dioxin conferences are published in the following years; so at least 33 contributions from the Toronto conference have to be added to the 1990 number. And another 22 for this meeting in Bayreuth. From the above table it can be seen that concern about the occurrence of dioxins in the pulp and paper production and resul-

ting possible risks to environment and humans started about 3 years ago and probably reached its peak in 1989.

STATUS: PAST - *PRESENT* - *FUTURE*

Discussions started about the release of halogenated organic chemicals into the environment in the course of the National Dioxin Study in 1987 [1], when the pulp and paper industry was associated with the presence of chlorinated organic compounds and especially dioxins.

The formation of dioxins in the pulping process using chlorine bleaching can be proven analytically, when, from precursors, a characteristic bleaching pattern can be identified. A typical isomer pattern of Cl_4DF and Cl_4DD found in the effluents of a pulp mill differs from that from a municipal waste incinerator: the typical incineration pattern contains characteristically the 1,3,6,7-Cl_4DF and 1,3,7,9-Cl_4DF and only minor amounts of the "toxic" 2,3,7,8-substituted compounds whereas the pulp mill effluent is dominated by the 2,3,7,8-Cl_4DF, 1,2,7,8-Cl_4DF, and 2,3,7,8-Cl_4DD isomers [2]. Occasionally, 1,3,6,8- and 1,3,7,8-Cl_4DD are the dominating isomers.

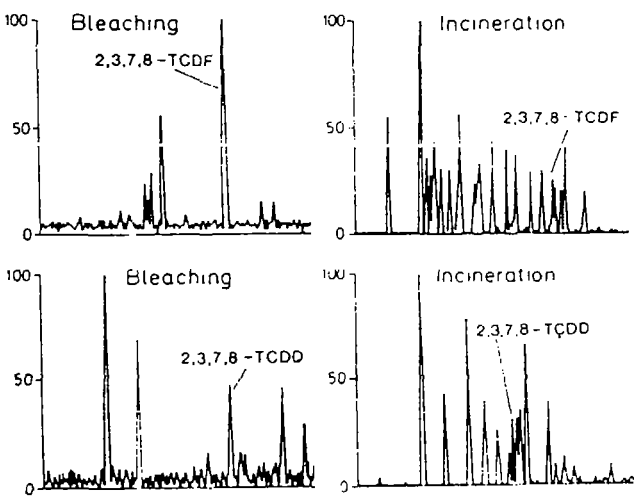

Fig. 1: Comparison of Cl_4DF and Cl_4DD patterns in a spent-bleaching liquor and in a typical incineration sample (from Ref. 2)

At Dioxin'89 in Toronto Clement et al. [3] reported that the highest levels of tetrachlorinated dioxins and furans were found in the bleached Kraft mills, whereas higher levels of the higher chlorinated PCDD/PCDF were detected in other process mills (including bleached Kraft-sulfite, semi-bleached Kraft, semi-chemical mechanical pulping, and groundwood).

RELEVANCE OF DIOXIN LEVELS DURING MANUFACTURE AND IN PRODUCTS

Problems Arising

a) Environmental impact through chloro-organics (mainly effluents)
b) Migration/mobility of PCDD/PCDF from packaging into food, e.g. milk cartons and thereby human exposure
c) Paper as waste (dumping, incineration).

Present Demands

Bleaching is not a question of aesthetics but is a form of purification. Furthermore there is still a public demand for bleached pulps because of its improved quality, e.g. colour, brightness, stability, tensile strength, softness, absorptivity, stiffness, cleanliness, etc.). Unbleached pulps are mostly used as newsprint and in packaging.

For softwood Kraft pulps, bleaching is generally performed by successive treatments with chlorine (C_1), alkali (E_1), chlorine dioxide (D_1), alkali (E_2), and chlorine dioxide (D_2). Sometimes, a hypochlorite stage (H) is inserted between E_1- and D_1-stages. Typical prebleaching conditions (C_1- and E_1-stage) in 1988 were:

C_1-stage: pulp (slurry consistency ~3%) is treated with about 60-70 kg elemental chlorine/ton of pulp at a temperature of 15-20 °C; the final pH is 1.5-2.0.
E_1-stage: chlorinated pulp (consistency ~10%) will be extracted with 35-40 kg alkali/ton of pulp at a temperature of 55-70 °C; the final pH is about 11.

The Various Bleaching Chemicals Are:

- Hypochlorite in various forms and chlorine (Cl_2): inexpensive, non-specific;
- Chlorine dioxide (Cl_2O): more expensive, difficult to handle, selective;
- Hydrogen peroxide (H_2O_2), molecular oxygen (O_2) used as brightening agents, included in alkaline stages; oxygen is mostly used before the first bleaching stage = oxygen prebleaching: expensive, special equipment necessary.

They can be used in one or more chlorination stages and an equal number of alkaline extraction stages.

Disadvantage: Due to the large amount of chemicals and the large volumes of water used in chemical pulping, the pulping industry has a potentially significant impact upon the local aquatic environment. Most interest has been focussed recently on the chlorine-bleaching of pulp rather than the actual pulping process [4].

PCDD/PCDF Levels During Pulping

In a Swedish survey, dioxins were detected in the low ppq-range (5 to 90 pg N-TEQ/kg of total effluent samples, including liquid and fine particulate) [4]. In the United States 2,3,7,8-Cl_4DD and 2,3,7,8-Cl_4DF were not detected in the processing water of pulp mills and 2,3,7,8-Cl_4DD was not found in unbleached pulp (detection levels at 0.3-1.0 ng/kg); however, 2,3,7,8-Cl_4DF was found in three unbleached kraft pulps in the 1 to 2 ppt range, but was not detected in four others [5].

PCDD/PCDF Levels in Final Pulp and Finished Paper Products

Typical levels of PCDD and PCDF found in Swedish Kraft bleached pine pulp were 5-15 ppt Nordic TEQ and 1-5 ppt Nordic TEQ in birch pulp [6]. During the 104 Mill Study [5], 2,3,7,8-Cl_4DD was found in 7 of 9 bleached pulp samples (on the basis of dry weight: median: 4.9 ng/kg) and 2,3,7,8-Cl_4DF in 8 of 9 samples (median: 50 ng/kg). Within the recent Swedish Dioxin Survey [7] the highest levels of PCDD/PCDF have been found in recycled paper pulps, whereas the two sulfate paper pulps contained extremely low levels of PCDD/PCDF. The unbleached technical mechanical pulp and the unbleached sulfite process pulp both contained hepta-chlorofurans and octa dioxins and furans.

Although the Swedish Minister of Environment and Energy declared on June 20, 1988 that all consumer pulp and paper products should be "dioxin-free" (below 1 pg/g) the results of dioxin analyses showed that PCDD/PCDF were identified in all - bleached and unbleached - paper products. Generally the levels in the unbleached samples were lower than in the corresponding bleached products. However, PCDD and PCDF could also be determined in products advertised as "dioxin-free" or "chlorine-free" [8] (see Table 2).

Table 2: Levels of PCDD/PCDF in various pulps [7] and consumers' paper products (pg/g of product) [8]

Pulp	N-TEQ	Paper products	N-TEQ
Recycled pulp	3.7	Diapers	1.0
	4.2	Cloth diapers (unwashed)	<0.2
Sulfate paper pulp (softwood)	0.2	Unbleached shopping bag	1.9
Sulfate paper pulp (hardwood)	0.1	Bleached shopping bag	5.7
Technical mechanical pulp	1.3	Cigarette paper	4.4
Unbleached sulfite pulp	0.6	Tampons	0.3
		Cotton	0.4
		Unbleached coffee filter	3.8
		Bleached coffee filter	8.2
		Carboxy-methyl Cellulose	<0.1

ACTIONS UNDERTAKEN TO REDUCE ENVIRONMENTAL IMPACT

Whereas in 1988 the bleaching of a softwood Kraft pulp generally resulted in the discharge of about 4-5 kg of organically bound chlorine per ton of pulp, a modern plant generates 1.5-2.0 kg TOCl/ton of bleached pulp. In Sweden new regulations will reduce the amount further to 0.1 kg TOCl/ton pulp.

The consumption of molecular chlorine, expressed as the ratio between chlorine and the lignin content (Cl_2-multiple) is the most important parameter in the generation of dioxins. Formation of PCDD and PCDF increased drastically above a critical value of about 0.15; below that level the formation was either non-existent or barely detectable [9]. The main decrease in the total amount of PCDD/PCDF when decreasing the Cl_2-multiple is mainly due to the reduction of tetrachlorinated congeners.

The practical action steps taken to reduce the generation of dioxins and chloro-organics, in US, Canada, and Scandinavia have included the following suggestions [10]:

1) To decrease the chlorine multiple to below 0.15 by increasing the level of chlorine dioxide substitution in the chlorination stage;
2) To minimize the entry of precursors into the bleach plant by careful selection of process additives and by efficient washing such as that obtained during oxygen bleaching.

Further, the following methods have been suggested from a limited small scale experimental database [8]:

1) To use first chlorine and then chlorine dioxide;
2) To decrease the concentration of chlorine by multiple additions or by decreasing consistency in the C-stage;
3) To increase the pH, thereby possible decreasing chloride ion concentration in the C-stage
4) To increase the C-stage temperature.

A further recommendation has been made by NCASI* that mill operators should only be provided with defoamers based on virgin oil [7]. This is a further method of reducing the entry of dioxin precursors into the mill.

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* National Council of the Paper Industry for Stream and Air Improvement, Inc. (USA)

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