Minimizing dioxin formation in mill-scale bleaching of softwood kraft pulp

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Since 1986, Värö Bruk has successively modified its bleaching process to decrease the discharge of chlorinated organic compounds to receiving waters.

Introduction

Background

In the autumn of 1985, information arrived from the United States suggesting that sludge from mills producing bleached chemical pulp may contain detectable quantities of polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) (*1–3*). 2,3,7,8-Tetrachlorinated dibensodioxin (TCDD) has also been found in fish caught downstream from pulp mills (*2*). This initiated investigations within the framework of the Swedish Forest Industries Water and Air Pollution Research Foundation (SSVL) to verify these findings.

As these investigations began, we discovered that crabs caught in the receiving waters outside the effluent tube at Värö Bruk contained increased levels of PCDDs and PCDFs (*4*). These new results initiated the SSVL Miljö 90 Dioxin Project, which hoped to clarify whether such compounds may form in pulp bleaching and, if so, to develop ways of minimizing their formation. The Dioxin Project included tests in both laboratories and mills. Most of the mill tests were carried out at Södra Skogsägarna's Värö Bruk mill.

The SSVL laboratory tests led to the following recommendations for reducing PCDDs and PCDFs:

- Thoroughly purify raw water and, if possible, avoid chlorination.
- Introduce oxygen bleaching.
- Thoroughly wash pulp prior to chlorination.
- Use low-multiple chlorination.
- Use efficient mixing in chlorination.
- Maintain good process control in chlorination.
- Minimize recirculation of C-stage backwater.

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Since 1986, Värö Bruk, as well as other Swedish bleached kraft pulp mills, has successively modified its bleaching process based on these principles. This paper summarizes the results obtained at the Värö mill.

Description of mill

Värö Bruk produces fully- and semi-bleached softwood kraft pulp with a production capacity of 300,000 a.d. tons/year.

In 1986, the production line consisted of batch digesters, filter washers, and a conventional tower bleach plant operating according to the sequence (C95+D5)(EO)HDED for bleaching to a brightness of 90% ISO and according to the sequence C(EO)HD for bleaching to a brightness of 70% ISO. The effluent was treated in a primary clarifier before being piped 5 km for release into the receiving waters at Cattegat in the North Sea.

During the spring of 1988, extended delignification was installed. At the end of 1989, sequential bleaching with chlorine dioxide and chlorine was introduced. This, together with increased use of chlorine dioxide in the first bleaching stage and hydrogen peroxide enforcement of the first alkaline extraction stage, made it possible to bleach in a low-chlorine-multiple mode (*5*).

In February 1990, oxygen bleaching was installed. Since then the pulp has been bleached to a brightness of 90% ISO according to a (D30,C65+D5)(EOP)DED sequence. The main motive behind all modifications to the pulp mill was to fulfill the requirements of the authorities to reduce discharges to receiving waters. The mill's permit condition for total chlorinated organics (TOCl) is a maximum of 1.5 kg/a.d. ton (equivalent to approximately 2.0 kg AOX/a.d. ton).

Experimental

The mill investigations were carried out on eight separate occasions.

Table I shows the production conditions, charge of chemicals, and the general composition of the total mill effluent when samplings were made. Most samples were taken as composite samples over a period of eight hours.

I. Process and effluent conditions at different sampling times

	Sample data, yr/month							
	8609	8610	8703	8803	8904	9001	9003	9004
Pulp quality (ISO brightness), %	70	90	70	90	90	90	70	90
Kappa number								
Before O stage	29	29	31	31	27	27	28	28
After O stage	. . .						20	18
Chlorine multiple (Cl_2), % of a.d. pulp/kappa no.	0.22	0.19	0.20	0.15	0.16	0.11	0.10	0.08
D charge in C stage, % of active Cl	5	5	5	5	5	30	35	35
H charge, kg/a.d. ton	1	2	1	2	1	0	0	0
D1+D2 charge, kg/a.d. ton	14	20	16	24	20	15	12	25
NaOH charge in E stages, kg/a.d. ton	32	37	37	43	38	36	15	19
O_2/H_2O_2 charge in E stages, kg/a.d. ton	5/0	4/0	4/0	4/0	5/0	4/1	0/0	4/0
				Total mill effluent				
Effluent flow, m^3/day x 10^{-3}	118	108	107	104	109	112	99	105
pH	3.0	3.4	2.7	7.1	7.4	3.4	7.2	6.8
COD, kg/a.d. ton	111	85	91	89	79	79	54	62
AOX, kg/a.d. ton	6.5*	6.0*	6.3*	4.4	3.7	4.3	2.1	1.8
Chlorate, kg/a.d. ton				3.9	3.0	4.5	2.2	4.4

* Calculated from the charges of C, D, and H

Analytical procedures

PCDDs and PCDFs ("dioxins") were determined as described earlier (*4, 6*). In this work, TCDD equivalent factors (TEF) in accordance with the "Nordic" model are used (*7*). Here TEF "Nordic" means that concentrations are given as TCDD equivalents.

COD analysis was carried out according to Lange's Cuvette Test [DIN 38 409/41 and AOX in accordance with SCAN-W 9:89 (1989)].

All other analyses were carried out according to common methods, using SCAN methods where available.

Chlorinated phenolic compounds were determined as described by Starck *et al.* (*8*).

Results and discussion

Basic investigation of conventional bleaching

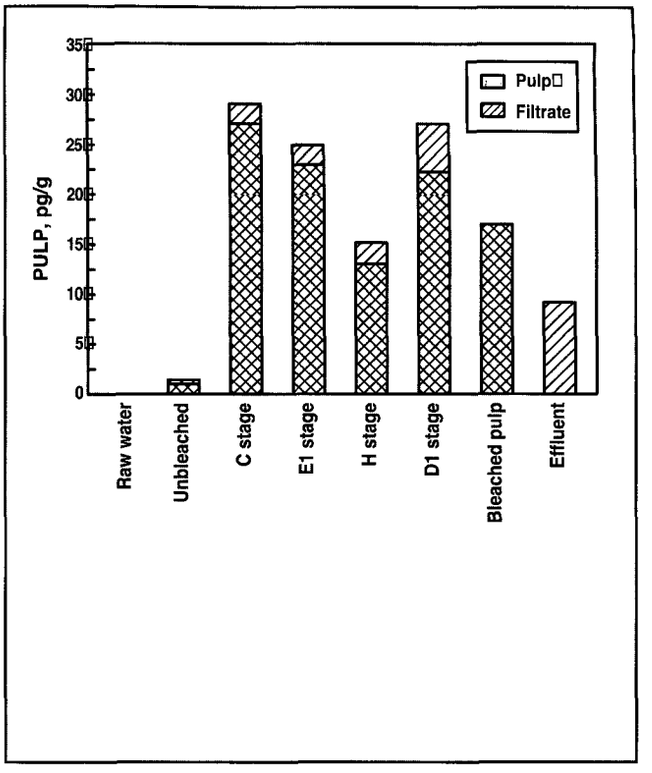
September 1986. The first samples were collected and ana-

II. Analysis of PCDDs and PCDFs (TEF "Nordic") in different samples

	Sample data	
	September 1986	October 1986
Raw water, pg/kg water	. . .	0.9
Total mill effluent, pg/kg water		
Water	14	43
Suspended solids	23	36
Total		3779
Unbleached pulp, pg/g	. . .	0.9
Pulp after C stage, pg/g	. . .	29
Pulp after E1 stage, pg/g	. . .	25
Pulp after H stage, pg/g	. . .	15
Pulp after D1 stage, pg/g	. . .	27
Final bleached pulp, pg/g	13	17
Sludge (primary clarifier), pg/g	2.6	. . .

pg=picogram

1. PCDDs and PCDFs (TEF "Nordic") in pulp samples and total mill effluent



lyzed to verify any formation of PCDDs and PCDFs. **Table II** summarizes the results. Significant quantities of dioxins in the total effluent were found. The compounds were present in the effluent's liquid phase as well as associated with the fines (suspended solids). The detected quantities correspond to a discharge of 5 µg/a.d. ton (TEF "Nordic") with the effluent water. With respect to the distribution of toxic PCDDs and PCDFs, it was clear that 2,3,7,8-TCDD and 2,3,7,8-TCDF were dominant.

Table II also shows that the bleached pulp contained dioxins. The quantities corresponded to a "discharge" of 13 µg/a.d. ton (TEF "Nordic"), and, again, 2,3,7,8-TCDD and 2,3,7,8-TCDF were dominant among the toxic dioxins.

In the sludge from the primary clarifier a "discharge" of 9 µg/a.d. ton was found.

October 1986. Based on the results from September 1986, we decided to repeat the study in more detail, using a greater number of sampling sites: raw water, unbleached pulp, pulp suspension after the C stage, pulp suspension after the E1 stage, pulp suspension after the H stage, pulp suspension after the D1 stage, final bleached pulp, and total mill effluent.

These results are also included in Table II. The quantities found in the total mill effluent and in the bleached pulp corresponded to a "discharge" of 27 µg/a.d. ton (TEF "Nordic"). Together with the results obtained in the first test (September), it was clearly shown that bleaching under such conditions will lead to the formation of dioxins. **Figure 1** suggests that by far the most dominating quantities of dioxins (TEF "Nordic") are formed in the C stage (*6*). This was later confirmed in extensive laboratory investigations (*9*).

Influence of improved washing

Normally condensates (from evaporation effects 4 and 5 and from the digesters) were used as washing liquid on the last washing filters. These condensates are among the most contaminated in the mill and could possibly represent a source of PCDD or PCDF precursors. We put it to the test in March 1987 by washing the unbleached pulp with hot and cold water instead of with condensates for a period of 48 hours. To achieve the best wash possible, the filtrate from the screening decker was also discharged to the sewer. The washing losses to the first bleaching stage were thereby reduced from 12 kg Na_2SO_4 to 9 kg Na_2SO_4 (total)/a.d. ton and, expressed as COD, from 15 kg/a.d. ton to 5.6 kg/a.d. ton. Otherwise, the production conditions were similar to those used in the basic investigation period discussed previously.

The results are shown in **Table III.** For comparison, the results of earlier analyses (October 1986) of similar samples using condensate as washing liquid are also included in the table. With regard to unbleached pulp, the contents of dioxins are, by and large, comparable.

After chlorination, however, the content was considerably lower for the water-washed pulp, particularly with respect to TCDF and peuta CDF. These results indicate that the modified washing procedure caused a reduced formation of PCDFs.

Later laboratory experiments confirmed this by showing that high levels of PCDFs may be formed in the chlorination of such condensates (*10*).

III. Influence of improved washing

Washing liquid	October 1986 Condensate: Unbleached pulp, pg/g	October 1986 Condensate: Pulp after C stage, pg/g	March 1987 Water: Unbleached pulp, pg/g	March 1987 Water: Pulp after C stage, pg/g
2,3,7,8-TCDF	6.8	100	1.8	26
Total TCDF	12	220	7.0	63
2,3,7,8-TCDD	<0.9	15	0.79	18
Total TCDD	ND	28	0.79	19
1,2,3,7,8-PeCDF	<0.7	15	0.58	5.2
2,3,4,7,8-PeCDF	<0.7	<0.5	<0.4	1.2
Total PeCDF	ND	61	0.58	20
1,2,3,7,8-PeCDD	<1	1.9	1.0	2.5
Total PeCDD	18	74	3.9	10.0
1,2,3,4,7,8-HXCDF	0.94	<0.2	<1	2.5
1,2,3,6,7,8-HXCDF	<0.5	0.2	<1	<0.5
2,3,4,6,7,8-HXCDF	<0.5	<0.2	<1	0.6
Total HXCDF	0.94	8.5	ND	14
1,2,3,4,7,8-HXCDD	<0.9	12	<1	0.94
1,2,3,6,7,8-HXCDD	<0.9	<1	<1	1.6
1,2,3,7,8,9-HXCDD	<0.9	7.8	<1	<0.5
Total HXCDD	15	63	ND	6.7
Total HpCDF	1.3	1.4	ND	15
Total HpCDD	9.5	22	6.1	19
OCDF	10	4.3	<10	79
OCDD	36	15	3.2	8.2
TEQ, TEF "Nordic"	0.9	29	1.5	23

ND = not detectable

IV. Influence of modified bleaching

	March 1988	April 1989	January 1990
Raw water, pg/kg water	1.1	...	...
Total mill effluent, pg/kg water			
Water	0.09	0.09	1.3
Suspended solids	80	14	5.8
Total	80	15	7.1
Unbleached pulp, pg/g			
Screening decker	2.2	...	...
Before C stage	10	...	...
Pulp after C stage, pg/g	4.7	...	...
Pulp after E1 stage, pg/g	14	...	...
Final bleached pulp, pg/g	4.6	1.0	0.84

V. Influence of oxygen bleaching

	March 1990	April 1990
Raw water, pg/kg water	...	0.02
Total mill effluent pg/kg water		
Water	...	0.01
Suspended solids	...	0.30
Total	3.2	0.31
Pulp after C stage	...	0.03
Final bleached pulp	0.07	0.03
Sludge (primary clarifier)	9.1	...

Influence of modified bleaching

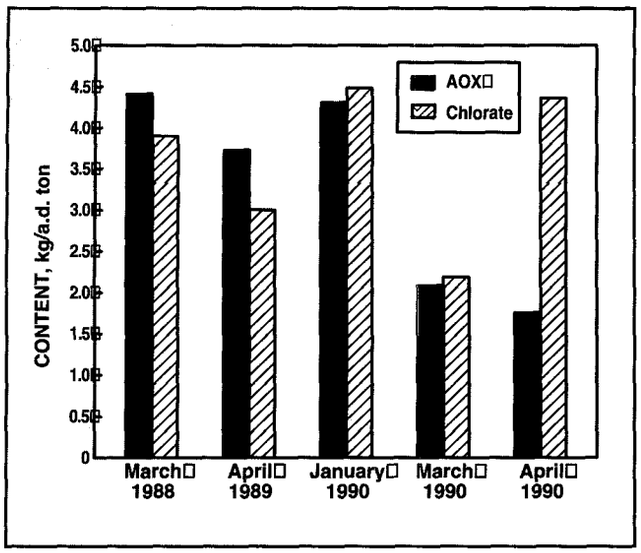
With reference to results obtained in laboratory investigations (*9*), three additional mill trials were carried out. The purpose of these trials was to check the influence of the following measures on the formation of PCDDs and PCDFs:

- Thorough purification of raw water and avoidance of chlorination
- Thorough washing of pulp prior to chlorination
- Low-multiple chlorination
- Efficient mixing in chlorination
- Good control of chlorine charging
- Minimal recirculation of C-stage filtrate.

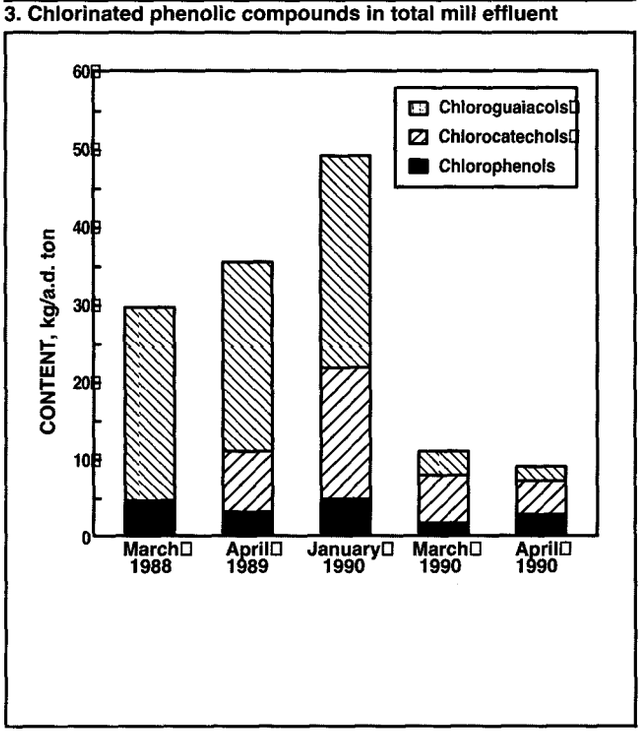
March 1988. In the March 1988 trial, the unbleached pulp was washed with water in the same way as in the trial in March 1987.

Twenty-four hours before sampling, the C stage was opened. Consequently, the backwater from the C filter, which is normally partly used for dilution of the pulp before the C stage, was released into the sewer and replaced with fresh

2. AOX and chlorate in total mill effluent



3. Chlorinated phenolic compounds in total mill effluent



water. The molecular chlorine multiple in the C stage was 0.15 (Cl_2, percent on a.d. pulp/kappa number).

April 1989. In the trial of April 1989, the production conditions were similar to those of the March 1988 trial except that the screening decker and the C stage were "closed."

Toward the end of 1989, the mill's capacity for producing chlorine dioxide was increased. At the same time, equipment was installed for sequential charging of bleaching chemicals in the C stage as well as enforcement of the E1 stage with hydrogen peroxide.

January 1990. These mill changes motivated a third mill trial, which was conducted during January 1990. Washing of the unbleached pulp was performed as in the April 1989 trial. The bleaching chemicals were charged using the sequence (D30,C65+D5) and a molecular chlorine multiple of 0.11. The conditions in the successive stages were adapted to the modified bleaching process (Table I).

All results obtained in these three trials are summarized in **Table IV.** These measures lead to an overall reduction in the formation of PCDDs and PCDFs of 90% or more as compared to conventional bleaching (Table II).

The highest degree of reduction was found in the trial utilizing sequential bleaching and the lowest chlorine multiple (January 1990). The effects are clearly visible in the bleached pulps as well as in the total mill effluents, with one exception. In the March 1988 trial, a disturbance in the primary clarifier increased the content of fines (suspended solids) in the total mill effluent to a level 10 times normal, masking the effect to some degree.

Influence of oxygen bleaching

In February 1990, the oxygen bleaching stage was put into operation. The succeeding washing equipment consists of a pressurized diffuser washer and a wash press. The O stage is based on medium-consistency technology. Before startup, the kappa number of the pulp before the O stage was 28; after startup, it was 18–20. The least contaminated condensate from the evaporation plant (effects 2 and 3) was used as washing liquid on the wash press.

Table I gives further operations data, including the chemical charges in the bleach plant. The molecular chlorine multiple was 0.10 and 0.08, respectively.

Table V shows that when adding oxygen bleaching and bleaching in the low-chlorine-multiple mode, the levels of PCDDs and PCDFs are very low, approaching the detection limit of dioxin analysis. The levels found correspond to a total "discharge" (total effluent, clarifier sludge, and bleached pulp) of 0.2–0.4 µg/a.d. ton (TEF "Nordic").

Discharge of chlorinated phenolic compounds, AOX, and COD

In addition to PCDDs and PCDFs, some other environmental parameters in the total effluent from the mill were determined. **Figure 2** shows the levels of AOX and chlorate in the total mill effluent during the different trials. In **Fig. 3**, the content of chlorinated phenolic compounds is shown.

There has been a substantial decrease in all chlorinated phenolics.

Mill experiences

Quite a number of extensive measures have been carried through in the mill since 1988 (extended delignification, oxygen bleaching, modified bleaching including increased use of ClO_2). The total cost for these measures has been about SEK 255 million (US$ 40 million).

These investments were necessary to fulfill the permit conditions for TOCl (1.5 kg/a.d. ton) mandated by the authorities.

To keep the mill production capacity at 300,000 a.d. tons/

year, it was also necessary to expand critical parts of the recovery plant because of the increased black liquor load. The total additional investment cost was about SEK 230 million, of which approximately SEK 80 million can be regarded as a preinvestment because the mill was 17 years old by 1989.

The rebuilding of the mill was performed in steps during operation and normal maintenance stops, while the measures in the recovery boiler were performed during a prolonged production stop in May 1990.

Taking both the investment costs and the changed bleaching chemicals and energy costs into account, the total operation cost has increased to approximately SEK 300/a.d. ton compared to costs in 1985.

Between 1985 and 1990, pulp strength showed a small positive change.

Conclusions

Motivated by the demand to decrease the discharges of chlorinated organic matter—AOX in general and polychlorinated compounds in particular—Värö Bruk has implemented various measures to minimize the use of elementary chlorine.

As a result of this four-year effort, the discharge of AOX has decreased from 6–7 kg/a.d. ton to below 2 kg/a.d. ton. The COD discharge also has decreased substantially.

The introduction of these measures resulted in a drastic decrease in the formation of PCDDs and PCDFs in the bleach plant. The total formation of dioxins has been reduced from a level of 20–30 μg/a.d. ton to 0.2–0.4 μg/a.d. ton (TEF "Nordic"), equivalent to a reduction of about 99%.

In relation to the decrease in the molecular chlorine multiple, the decrease in the formation of PCDDs and PCDFs is larger than the corresponding decrease in discharges of AOX. Similar observations can also be made for chlorinated phenolic compounds (*9, 11–13*).

With a molecular chlorine multiple below 0.1, the formation of dioxins is practically eliminated. The observed concentrations of PCDDs and PCDFs in the bleached pulp now are on the same level as those found in unbleached pulps (*14*).□

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