Reducing discharges from sulfite pulp bleach plants

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New bleaching sequences substantially reduced AOX and EOX in the effluent and in the pulp without significantly altering pulp quality.

Pulp mill bleach plant discharges are known to contain organochlorine compounds which are potentially harmful to the environment (*1*). These compounds show a wide range of effects on aquatic organisms, including weakly acute toxicity or genotoxicity, sublethal effects, and varying degrees of persistence (*2*). The lipophilic compounds may show a potential to bioaccumulate (*3*). Effluent discharges are monitored and regulated worldwide, and the allowable discharge of organochlorine compounds per ton of pulp is steadily dropping.

Limiting the discharge of organochlorine compounds may be achieved by reducing the chlorine demand during bleaching or by biological treatment of the effluent (*4-7*). Greater delignification during cooking or using alternative oxidizing agents in the bleaching sequences have both been proven to be effective methods for reducing the chlorine demand of pulp (*8-10*).

Most of the extensive studies carried out on bleach plant effluents and investigations of more acceptable bleaching processes have focused on kraft pulps, and a linear relationship has been established between chlorine demand and quantity of organochlorine compounds formed during bleaching of this type of pulp (*8, 11*).

Although sulfite pulp production is decreasing, the quantity produced is still considerable. This is especially true in Norway, where half of the bleached chemical pulp is sulfite and 50% of this is dissolving pulp.

Dissolving-grade pulps have a low lignin content, and the quantity of chlorinated lignins derived during bleaching should be correspondingly low. However, sulfite pulps contain greater quantities of wood resins, which mainly consist of resin and fatty acids and esters of fatty acids. Some of these compounds are readily chlorinated during bleaching with chemicals containing chlorine.

Wood storage prior to sulfite pulping is commonly used to reduce the resin content, and this enhances the quality of the pulp as well as affecting the properties of the effluent from the bleach plant.

In an investigation some years ago, fairly high concentrations of organochlorine compounds were found in the effluents from a mill producing dissolving sulfite pulp (*12*). The concentration of AOX (adsorbable organically bound halogen) and EOCl (extractable organically bound chlorine) were 3.6 kg/ton and 0.5 kg/ton of pulp, respectively.

In 1987, a project was started with the aim of reducing the discharges of organochlorine compounds and organic matter from three Norwegian sulfite mills. The project was a cooperative effort between research institutes, the Norwegian sulfite industry, and government, and it was divided into the following parts:

- Establish the state of the art with respect to sulfite bleaching.
- Determine the discharge concentration for each mill in 1987.
- Perform laboratory experiments with more environmentally acceptable bleaching sequences relevant to each mill, and evaluate product and effluent characteristics by chemical analysis and biological testing.
- Perform full-scale mill trials of the most promising bleaching sequences.

This article will concentrate on the mill results. Further information on this project can be obtained from the authors.

Experimental

There are three sulfite mills in Norway producing bleached pulp, and all of them participated in this project:

- Mill A produces 160,000 tons of calcium acid sulfite pulp, of which about half is dissolving grade.

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Bleaching process before 1989: D/CEHD. The proportions of chlorine dioxide and chlorine were 35/65 for dissolving-grade pulp and 50/50 for paper grade. Unbleached kappa numbers were about 8 and 18, respectively.

New bleaching process: DEHD for dissolving-grade and part of paper-grade pulp production. The other part is bleached with PP.

- Mill B produces 70,000 tons of magnesium acid sulfite dissolving-grade pulp.

  Bleaching process before 1989: CEH.

  New bleaching process: CPH.

- Mill C produces 50,000 tons of magnesium bisulfite paper-grade pulp.

  Bleaching process before 1989: The main part of the production was bleached with OCPH. Unbleached kappa number was about 24, 15–16 after the oxygen stage.

  New bleaching process: O(C+K)PK, where K denotes sodium chlorite.

Laboratory cooking and bleaching trials

Magnesium bisulfite cooking was carried out on three qualities of spruce chips: green wood (untreated), stored wood (12 days at 60°C and 85% relative humidity), and acetone extracted green wood. The raw material was cooked to three different kappa numbers.

Chlorination

Chlorination was at 3% consistency, 23°C, and lasted 40 min.

Alkaline extraction

Alkaline extraction was at 10% consistency, 60°C, and lasted 1 h. Charged NaOH = % chlorine × 0.2 + 0.4%.

Pulp characterization methods

Paper-grade pulps were analyzed using the following standard methods:

- Extraction with dichloromethane (resin content): SCAN-C7:62
- Brightness: SCAN-C11:75
- Kappa number: SCAN-C1:77
- Viscosity: SCAN-C15:88
- Alkali solubility: SCAN-C2:61
- Physical properties of laboratory sheets: SCAN-28:76.

Washable AOX. During paper production some of the chlorinated organic compounds in the pulp are leached out. This test gives an estimate of the amount of organically bound chlorine drained from the paper machine during paper production. Pulp (24 g) was preswollen in water (1 L) for two hours. More water (1 L) was added and the pulp disintegrated according to International Standards Organization (ISO) Standard 52630. After dilution to 8 L, the mixture was stirred for 10 min, and a sample of 500 mL was filtered through a nylon filter (24 μm). The pulp on the filter was dried and weighed, and the filtrate was refiltered through a GFA filter (11-cm-diam.). AOX on the last filtrate was determined according to SCAN-W9:89 and washable AOX calculated as the pulp weight contributing to AOX in the filtrate.

EOX in pulp. Pulp (12 g, air dried) was extracted in a soxhlet with cyclohexane/isopropanol (10:1) for 4 h. The solution was washed twice with water (pH 2) and dried with sodium sulfate. Chlorine content was determined by neutron activation analysis (*13*).

Dissolving-grade pulps were analyzed as follows:

- Extraction with dichloromethane (resin content): SCAN-C7:62
- Viscosity: SCAN-C15:88
- Alkali solubility: SCAN-C2-61.

The pulp's suitability as a raw material for viscose production was determined according to Ellefsen and Glersen (*14*) by measuring viscose viscosity and filtration ability.

Effluent analysis included:

- AOX: SCAN-W9:89

  COD_{Cr}: Norwegian Standard NS 4748.

Water sampling

Composite samples of the bleach plant effluents were taken over a period of 24 h. The samples were stored at 4°C prior to analysis or testing.

Analysis of AOX. AOX was determined by use of a Dohrmann-Envirotech DX 20 organic halogen analyzer (*15*). The samples were diluted 100 times, acidified (pH 2), and passed through two glass columns containing carbon. The amount of AOX was determined by microcolumetric titration after combustion of the carbon.

Analysis of extractable organically bound chlorine (EOCl). The pH of the water samples was adjusted to pH 2 with sulfuric acid. The sample was extracted twice in the sampling bottle with cyclohexane (50 mL/L) for 2 h using magnetic stirring. The cyclohexane phases were combined, washed with distilled water (pH 2) three times (3 × 25 mL), and dried over sodium sulfate (*15*). An aliquot was taken for determination of EOCl by neutron activation analysis (*12*).

Toxicity testing. Toxicity of all the mill effluents to the bacterium *Photobacterium phosphoreum* was assayed with Microtox®. The pH was adjusted to neutral by adding NaOH before testing. Microtox tests were used to measure toxicity of different fractions of wastewater and to investigate the persistence of toxicity.

The toxicity of the wastewaters from each bleaching stage in Mill B was tested on a marine algae (*Skeletonema costatum*) and a harpacticoid crustacean (*Nitocra spinipes*). In the algal toxicity test, the effect of the wastewater on the growth rate of the algae was examined in natural sea water enriched with nutrients and with different concentrations of wastewater added (*12*).

With *Nitocra spinipes*, the lethality was recorded during 96-h exposure to different concentrations of wastewater in natural sea water of 15 g/L salinity (*16*).

Results and discussion

The results of the laboratory investigation to establish the amount of AOX formed during chlorination of sulfite pulps

II. AOX in CE-filtrate and EOCl in pulp after CE-stage from laboratory bleaching experiments

Raw material	Kappa no.	DCM extraction, %	Chlorination factor	CE kappa no.	DCM extraction, %	% Cl in DCM extraction	kg EOCl/ton	kg AOX/ton	Total organochlorine, kg/ton	% EOCl of total organochlorine
Green wood	14.6	1.5	0.15	1.9	1.1	9	1.0	3.9	4.9	20
			0.20	1.0	1.3	14	1.8	4.7	6.5	28
			0.25	0.7	1.3	17	2.2	5.3	7.5	29
Stored wood	12.0	0.94	0.15	1.9	0.6	10	0.6	3.3	3.9	15
			0.20	1.1	0.6	14	0.9	3.9	4.8	18
			0.25	0.8	0.7	14	1.0	4.6	5.6	18
Acetone extracted green wood chips	15.9	0.46	0.15	2.0	0.4	13	0.5	5.0	5.5	8
			0.20	1.1	0.4	17	0.7	6.2	6.9	10
			0.25	0.8	0.4	18	0.7	7.0	7.7	9

I. AOX in CE-filtrate from laboratory bleaching experiments

Kappa no.	Chlorination factor	CE-kappa no.	kg AOX/ton	% AOX of charged chlorine
		Green wood		
9.0	0.15	1.9	2.5	18
	0.20	1.0	2.6	14
	0.25	0.7	3.5	16
14.6	0.15	2.8	3.9	18
	0.20	1.5	4.7	16
	0.25	1.0	5.3	14
19.9	0.15	3.6	5.3	18
	0.20	1.9	6.8	17
	0.25	1.2	8.7	17
		Stored wood		
7.9	0.15	1.4	1.9	16
	0.20	0.9	2.4	15
	0.25	0.6	3.3	17
12.0	0.15	1.9	3.3	18
	0.20	1.1	3.9	16
	0.25	0.8	4.6	15
19.6	0.15	2.7	6.1	21
	0.20	1.4	7.2	18
	0.25	0.9	8.4	17
		Acetone extracted green wood chips		
9.5	0.15	1.5	3.	22
	0.20	0.9	3.4	18
	0.25	0.7	3.6	15
15.9	0.15	2.0	5.0	21
	0.20	1.1	6.2	20
	0.25	0.8	7.0	17
24.8	0.15	3.0	6.5	18
	0.20	1.5	9.4	19
	0.25	0.8	12.8	21

are presented first. Then the results from mill experiments with old and new bleaching sequences are presented for each mill.

Chlorination of sulfite pulps

The results of this study are summarized in **Tables I and II**. Table I shows results from chlorination trials and AOX determination and Table II the relationship between AOX in the filtrate and EOCl in pulp after CE treatment, when the extractive content of unbleached pulp varies from 0.46% to 1.5%.

From these tables, we can conclude that an average of 16–17% of the charged chlorine is converted to organically bound chlorine in the filtrate from CE treatment. This means that chlorination of sulfite pulps from spruce gives considerably higher amounts of AOX in the CE filtrate than chlorination of kraft pulps from softwood. At the same kappa number, the amount of chloroorganics formed during the chlorination stage of sulfite pulps is almost twice that found during corresponding chlorination of kraft pulps.

Further, the amount of resin in unbleached pulp has little influence on AOX in CE filtrate but is a decisive factor for the amount of chlorinated extractives retained in the pulp.

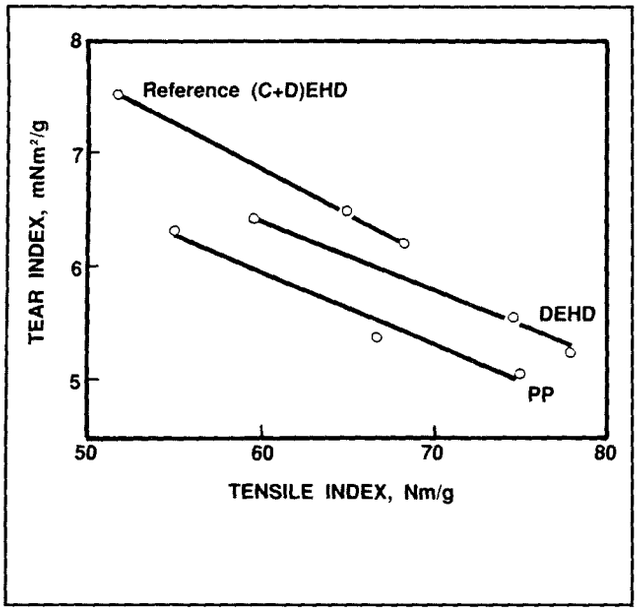
Mill A

During 1989, the bleaching process was changed and elemental chlorine was replaced by chlorine dioxide. In addition, a new tissue line was started where the pulp was bleached with a two-stage peroxide sequence. Pulp properties before and after process changes were analyzed, and for both dissolving and paper-grade pulps the properties changed very little. As expected, the tissue pulp had lower brightness (about 78% ISO) and lower brightness stability. The strength properties of the paper-grade pulp and the tissue pulp can be seen in **Fig. 1**, which shows that a certain reduction in the tear index took place when switching to the new bleaching process.

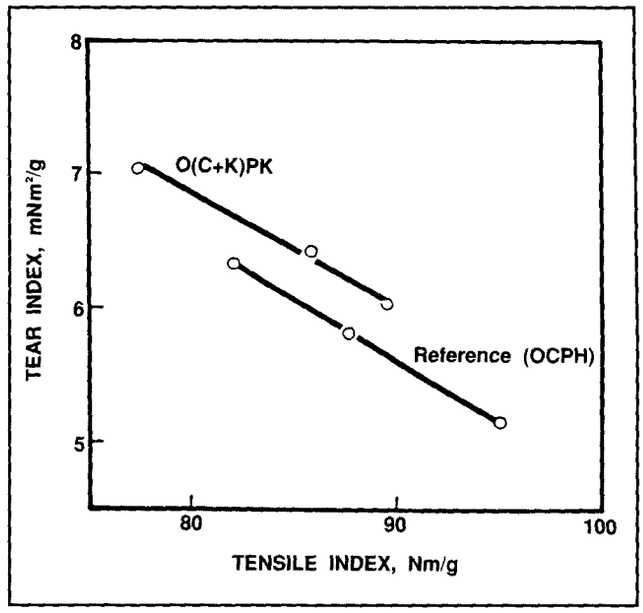
Pulp mill effluent discharge and organochlorine content in pulp are shown in **Table III**. A large reduction in AOX in the effluent was found for both pulps when all the elemental chlorine was replaced by chlorine dioxide. A similar reduction was observed for EOX.

The COD discharge from the dissolving pulps increased

1. Strength properties of paper-grade pulps from Mill A before and after process change



2. Strength properties of pulp from Mill C before and after process change



III. Discharge concentrations and organochlorine concentrations in pulp from tests at Mill A

		Discharge					Pulp	
Pulp	*Bleaching sequence*	*Chlorine, %*	*AOX, kg/ton*	*EOCl, kg/ton*	*COD, kg/ton*	*TOC, kg/ton*	*EOCl, g/ton*	*Washable AOX, g/ton*
Dissolving grade	Old (D/C) EHD	1.0	3.8	0.2	160	60	*	*
	New DEHD	0	1.2	0.06	220	88	*	*
Paper grade	Old (D/C) EHD	1.7	3.6	0.1	85	35	193	48
	New DEHD	0	1.1	0.1	74	20	120	43
	New PP	0	0.02	0.002	70	23	8	2

*Not analyzed

IV. Discharge concentrations from tests at Mill B

Bleaching sequence	*Chlorine, %*	*AOX, kg/ton*	*EOCl, kg/ton*	*COD, kg/ton*	*TOC, kg/ton*
Old CEH	1.2	3.5	0.5	*180*	62
New CPH	0.6	1.7	0.1	*150*	50

V. Viscose production parameters for pulp from Mills A and B

	Old bleaching sequence		*New bleaching sequence*	
Source	*Viscose viscosity*	*Kf*	*Viscose viscosity*	*Kf*
Mill A	49	11.7	49	9.5
Mill B	40	8.9	40	8.9

VI. Discharge concentrations and organochlorine concentrations in pulp from tests at Mill C

Bleaching sequence	Chlorine, %	Discharge AOX, kg/ton	Discharge EOCl, kg/ton	Discharge COD, kg/ton	Discharge TOC, kg/ton	Pulp EOCl, g/ton	Pulp Washable AOX, g/ton
Old OCPH	2.6	6.0	0.3	80	35	550	60
New O(C+K)PK	1.6	1.8	0.04	95	35	430	70
New P	0	0.07	0.01	*	34	*	*

*Not analyzed

with the new bleaching sequence. The paper grades showed a reduction in COD on converting to chlorine dioxide bleaching. This reduction in organic matter discharge mirrors similar investigations on kraft pulps (*9*).

Mill B

During 1989 the mill reduced its elemental chlorine consumption by 50%, replacing it with peroxide. This led to a reduction in organochlorine discharge as measured by AOX and EOX (**Table IV**), which was in good agreement with results from the laboratory trials.

The discharge of organic matter decreased somewhat with the new bleaching sequence. This was not expected because the discharge was not thought to be influenced by the new bleaching sequence. However, a reduction of about 15% was found.

The dissolving pulps with the new bleaching sequences from both Mill A and Mill B were tested for suitability as the starting material for viscose production. These results are summarized in **Table V** and show highly satisfactory values for Kf (viscose filtration factor) and viscose viscosity for the new bleaching sequences. As far as could be determined, the quality of the pulp with regard to this purpose remained unchanged.

Mill C

During 1989, the use of elemental chlorine was reduced by about 40% by introducing sodium chlorite (K) in the chlorination stage. Previously hypochlorite had been used in the final stage, and now this was also replaced with sodium chlorite.

The mill has also installed a new line with a one-stage peroxide bleached pulp.

As expected, the introduction of chlorite in the bleaching sequence yielded pulp with higher bleached viscosity and better tearing strength, as shown in **Fig. 2**.

The reduction in discharged organochlorine compounds was larger than could be expected from the reduction in elemental chlorine (**Table VI**). The replacement of the final hypo stage with chlorite is also beneficial in reducing the total AOX load. Discharges of COD and total organic carbon were comparable for the old and new bleaching sequences.

The reduced chlorine charge did not give a similar reduction in organochlorine concentration in the pulp. The EOCl concentration was reduced by about 20%, but the washable AOX concentration increased somewhat.

The amount of dichloromethane extractives was not affected by the new bleaching sequences for any of the mills. The high content of EOX found in sulfite pulps is attributable to the relatively higher extractive content. For kraft pulps, the EOX fraction in the effluent has been reported to be between 0.5% and 2.5% of the AOX (3.14). In this investigation, EOX contents of about 5% of the AOX values were found.

The dioxin discharge from the mills were measured for the old bleaching sequences, and these results are shown in **Table VII** together with results from a reference kraft mill. The discharge from the sulfite mills appears to be lower by a factor of 20 or more (*17*). Since the initial values were so low, further measurements were not taken.

Biological testing

All the spent bleach liquors investigated were tested for toxicity with Microtox. The discharges from all the old bleaching sequences were about equally toxic to the bacterium. The EC_{50} value was between 2% and 6% spent bleach liquor. The new bleaching sequences were found to be somewhat more toxic to the bacterium. For these discharges, the EC_{50} values were between 0.2% and 2% spent bleach liquor.

For Mill B, more extensive testing was performed. Each of the three bleaching stages were tested with an alga and a harpacticoid crustacean.

The EC_{50} values for the growth rate of *Skeletonema costatum* and the LC_{50} values for *Nitocra spinipes* in the

VII. Discharge of chlorinated dioxins using the "old" bleaching sequence

Mill	Old bleaching sequence	Discharge, µg/ton	Total discharge/ yr, mg
A	D/C EHD 35/65	0.3	40
B	CEH	0.4	25
C	OCPH	0.5	25
Kraft mill	D/C EDCED 40/60	12	2600

VIII. EC_{50} and LC_{50} values of the effluent tested

	EC_{50}, mL/L		LC_{50}, mL/L	
	Old	New	Old	New
Chlorination	60	>100	90	130
Alkaline extraction	17	20	80	100
Hypochlorite	100	>100	>560	>560

effluents from each bleaching stage in both the "old" and "new" processes are shown in **Table VIII**.

The toxicity tests show that the wastewater from the alkaline extraction stage was the most toxic and the hypochlorite wastewater the least toxic to both test organisms. The chlorination and alkaline extraction wastewaters from the "new" process were less toxic than from the "old" process, but the difference was not very large. The toxicity of the hypochlorite wastewater was too low to allow calculation of EC_{50} and LC_{50} values. The lethality of *Nitocra* at the highest tested concentration (560 mL/L) was, however, slightly higher in the "old" wastewater than in the "new" (24% and 20%, respectively).

The toxic effects of the different wastewaters were lower than previously found (*12*). The test results for Mill B are contradictory. In the Microtox test, the toxicity was slightly higher for the new bleaching processes. For the other two test organisms, the new process was slightly less toxic than the old process. This confirms the previous observations that compounds other than the organochlorines are the main contributors to the toxicity of spent bleach liquors.

From the environmental point of view, it is the highly lipophilic organochlorine compounds with a possibility to bioaccumulate that are of greatest concern. The most lipophilic fraction of the EOCl has been isolated for some of the spent bleach liquors (*15*). Between 20% and 80% of the organically bound chlorine in EOCl was bound to highly lipophilic compounds. Reducing the chlorine charge will reduce the proportion of highly chlorinated compounds, thereby reducing the lipophility of the compounds in the EOCl extract (*18*).□

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CORRECTION

Author omitted from paper on biotechnology

In "Biological treatments as an alternative to chemical pretreatments in high-yield wood pulping" on p. 189 of the March 1991 issue, one of the authors, T. Kent Kirk, was omitted. Kirk is the director of the Institute for Microbial and Biochemical Technology, USDA Forest Service, Forest Products Laboratory, One Gifford Pinchot Dr., Madison, Wis. 53706.

Tappi Journal regrets any inconvenience due to this error.