Laboratory reduction of chloro-organics during bleaching of kraft pulps by continuous addition of chlorine and chlorine dioxide

Nipun Marwah, Thomas W. Joyce, C.-L. Chen, Josef S. Gratzl
Dept. of Wood and Paper Science, North Carolina State University, Raleigh, NC 27695

ABSTRACT *A simple modification of an unbleached kraft pulping operation to chlorine bleaching was studied with the objective of reducing the formation of chloro-organics. The method involves the continuous dropwise addition of chlorine or a mixture of chlorine and chlorine dioxide. About 50% reduction in chloro-organics, including AOX and monomeric chlorinated phenols, could be achieved by dropwise addition of a 50:50 mixture of chlorine and chlorine dioxide, as compared to the conventional addition of a single charge. The reduction in chloro-organics results from a low concentration of chlorine contacting the pulp, a condition that favors oxidation over substitution reactions.*

The response of an oxygen-bleached kraft pulp to this treatment was also studied. This pulp was not as responsive as the unbleached pulp, apparently because of the low content of free phenolic lignin structures in the oxygen-bleached pulp.

Chlorination of the ethanol-extracted unbleached pulp and the ethanol extract showed that low-molecular-weight lignin degradation products extracted by ethanol contribute substantially to the formation of chloro-organics.

KEYWORDS
Adsorbable organic halogens
Bleach plants
Chlorination
Chlorine compounds
Effluents
Kraft pulps
Loads
Organic compounds
Phenols
Reduction

The formation of chloro-organics in the bleaching of pulp with chlorine has been of increasing public concern because toxic compounds are present in the bleach effluents. Earlier studies did not show any evidence of the presence of polychlorinated dibenzo-dioxins (PCDDs) and dibenzofurans (PCDFs) in bleach plant effluents and paper mill sludges. However, with the use of analytical techniques that are more sensitive, extremely minute amounts of these compounds, on the order of parts per trillion or quadrillion, could be detected, including the very toxic 2,3,7,8-tetrachlorinated isomers (*1–3*). These compounds are predominantly formed in the chlorination stage (*2*).

As a consequence, considerable efforts have been made to reduce the formation of chloro-organics in general and of PCDDs and PCDFs in particular. The following approaches have been taken:

- Reduction in the chlorine charge
- High substitution (>50%) of chlorine by chlorine dioxide
- More efficient brownstock washing
- Use of chlorine-free alternatives based on oxygen, hydrogen peroxide, and ozone.

Swedish researchers were the first to show a relationship between the active chlorine applied and the amount of 2,3,7,8-TCDD or 2,3,7,8-TCDF formed (*2*). Kringstad *et al.* suggested lowering the chlorine factor to less than 0.15 as one of the control measures (*4, 5*). The chlorine factor (*CF*) defines the ratio of chlorine to lignin in the first stage of bleaching using the kappa number as a measure of the lignin content of the pulp:

$$CF = \%\ Cl_2 \text{ on pulp/ kappa no.} \quad (1)$$

Axegard *et al.* found that the formation of chlorinated organics is

proportional to the amount of chlorine charged to the pulp (*6-7*). In earlier studies, Liebergott examined the alternatives of adding chlorine water continuously over various lengths of time and of splitting the chlorine dosage into two portions (*8*). With chlorine added by either of these alternative modes, the formation of chlorophenols could be substantially reduced. Recently, Hise showed that splitting the chlorine charge into two and three doses lowers 2,3,7,8-TCDF by about 70% and 2,3,7,8-TCDD by about 50% (*9*). These studies have demonstrated that keeping the chlorine concentration low throughout the treatment can substantially reduce the formation of chloro-organics, including polychlorinated dibenzodioxins and dibenzofurans. The reduction in the formation of chloro-organics is apparently caused by the lower rates of chlorination reactions (electrophilic substitution) at the lower chlorine concentrations.

Another approach to reduce the formation of chlorinated organic compounds is the substitution of chlorine by chlorine dioxide as demonstrated by Reeve (*10*), Axegard (*11*), Annergren (*12*), and Germgard (*13*). In the presence of chlorine dioxide, oxidative processes are favored over substitution reactions, which leads to reductions in the formation of chloro-organics.

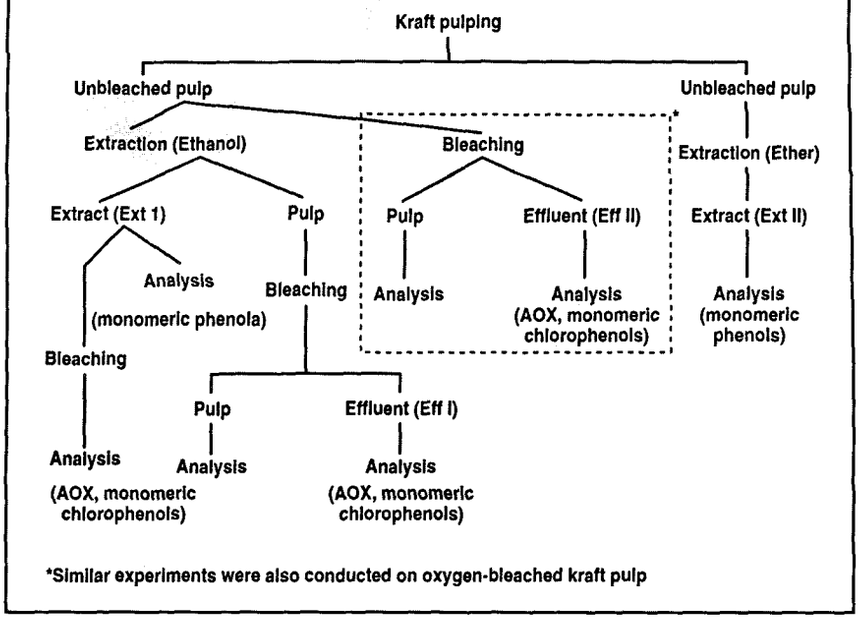
Our objective in this study was to reduce the formation of chloro-organics by following the concept of gradual addition of chlorine as originally proposed by Liebergott (*8*) and to extend this approach to the addition of mixtures of chlorine and chlorine dioxide. Conventional (one charge) and modified (continuous addition) bleaching experiments were conducted with unbleached and oxygen-bleached kraft pulps and with the ethanol-extracted unbleached kraft pulp conventional (one charge) bleaching experiments were conducted on the ethanol extract. The formation of chloro-organics was monitored by the formation of selected monomeric chlorinated phenols and the adsorbable organic halogen compounds (AOX).

Results and discussion

Chlorination of unbleached pulp

The experimental outline for this study is presented in **Fig. 1. Table I**

1. Flow chart of the experiment



*Similar experiments were also conducted on oxygen-bleached kraft pulp

I. Chlorination of unbleached kraft pulp at different chlorine factors

Chlorine factor	*Initial kappa no.*	*CE kappa no.*	*Δ kappa no.*	*Total AOX, kg/metric ton*	*AOX/ Δ kappa no.*
0.10	32.6	17.5	15.1	1.3	0.09
0.15	32.6	10.8	21.8	3.1	0.14
0.25	32.6	4.6	28.0	6.6	0.24

Bleaching conditions: 40°C, 1 h, 2.5% consistency.

II. Chlorophenols in C-stage effluents at chlorine factors of 0.10, 0.15, and 0.25

	Concentration, g/o.d. metric ton		
Compound	*0.10*	*0.15*	*0.25*
p-Chlorophenol	...	...	...
2,4,6-Trichlorophenol	1.6	5.1	6.3
2,3,4,6-Tetrachlorophenol	0.1	0.6	0.7
4-Chloroguaiacol	...	...	...
4,5- and 4,6-Dichloroguaiacol	7.0	9.0	13.1
3,4,5-Trichloroguaiacol	0.1	0.3	0.5
4,5,6-Trichloroguaiacol	0.1	0.5	2.0
Tetrachloroguaiacol	0.3	0.8	1.8
mono Chlorocatechol	...	...	...
Dichlorocatechol	...	...	...
Total	9.2	16.3	24.4

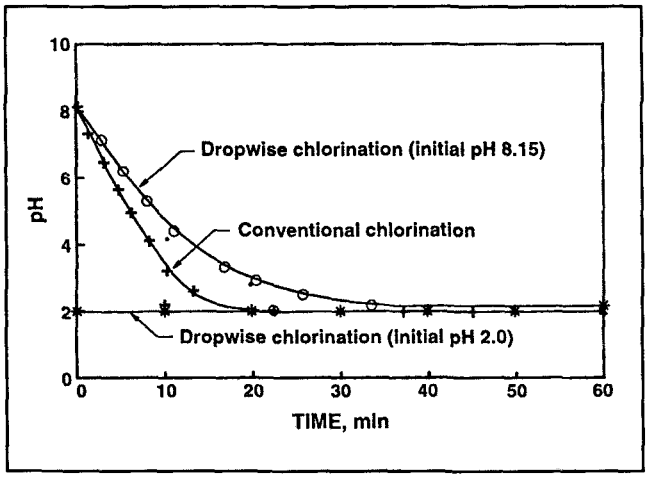
Conditions: 40°C, 1 h, 2.5% consistency.
Ellipses indicate negligible amounts.

III. Chlorination of unbleached kraft pulp at a chlorine factor of 0.15 (100% chlorine)

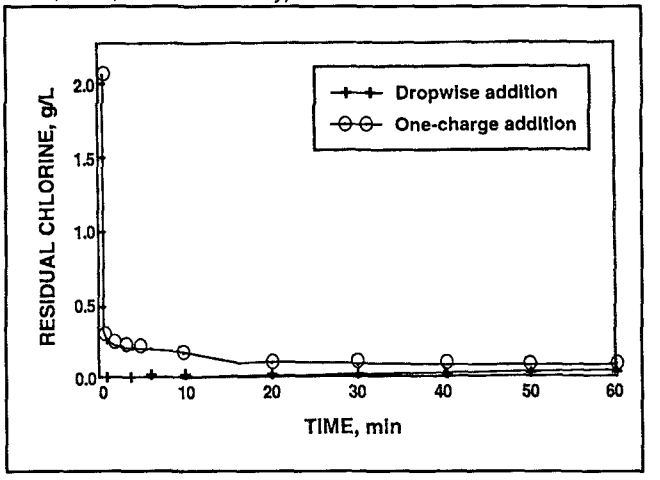
Addition method	Initial pH	Initial Kappa no.	C stage Kappa no.	C stage AOX, kg/metric ton	C stage AOX/ Δ kappa no.	E stage Kappa no.	E stage AOX, kg/metric ton	E stage AOX/ Δ kappa no.	CED viscosity, mPa•s
One charge	...	32.6	22	2.2	0.21	10.8	0.9	0.08	23.4
Dropwise	8	32.6	23	1.1	0.11	11.4	0.5	0.04	24.4
Dropwise	2	32.6	23	1.3	0.12	11.2	0.6	0.05	25.3

C stage: 40°C, 1 h, 2.5% consistency.
E stage: 70°C, 10% alkali, 5% consistency.

2. The pH profile during chlorination



3. Chlorine profile in one-charge and dropwise additions (0.25 chlorine factor, 40°C, 2.5% consistency)



presents the effects of different chlorine factors (using conventional chlorination) on delignification and on the formation of chloro-organics (AOX). **Table II** presents the effects of different chlorine factors on the formation of monomeric chlorophenols.

As shown in Table I, AOX increases with the chlorine factor, particularly at a chlorine factor of greater than 0.10. A similar observation was reported by Axegard *et al.* (*6, 7*). The table also shows the AOX formation efficiency during delignification, expressed as AOX formed per unit of lignin (kappa number) removed. The amount of chloro-organics generated per unit of lignin removed increases substantially (by about 55%) when the chlorine factor is increased from 0.10 to 0.15. At a higher chlorine charge, the efficiency of AOX production increases further to about 71% higher than the amount obtained at a chlorine factor of 0.15.

Table II shows the change in monomeric chlorophenols with chlorine concentration. The yields of the individual phenols increase with the chlorine factor but at somewhat different rates. The rather high yields of chlorinated phenols as compared to guaiacols suggest the presence of a substantial amount of compression wood in the furnish. Compression wood lignin contains rather substantial amounts of *p*-hydroxyphenylpropane structures.

The content of monosubstituted derivatives is very low for all three types of phenols (phenols, guaiacols, and catechols). While dichlorophenols are practically absent, the content of dichloroguaiacols is extremely high. Noteworthy is the rather high content of 4,5,6-trichlorophenol.

Table III presents the results obtained from chlorinated kraft pulp for which we employed a chlorine factor of 0.15. About one half of the degraded lignin, representing about two thirds of the AOX components, is soluble in the acidic chlorination (C stage) effluent. The other half is only soluble in base (first E-stage effluent), and it carries the remaining portion of the chloro-organics, predominantly substances of high molecular weight (*14*).

As **Fig. 2** shows, the pH profiles for the two modes of chlorination are

quite different. As expected, the pH drop in the initial phase for dropwise addition was less pronounced for the one-charge addition, and it took much longer to level off at pH 2. This means that for a considerable period of time (up to 20 min) the pH of the pulp suspension was over about 3, a pH level where one might expect substantial pulp damage as a result of the higher concentration of hypochlorous acid in bleach. On the other hand, the chlorine concentration in dropwise addition is very low (less than 0.05 g/L), and it remains constant throughout the treatment (**Fig. 3**).

In one-charge addition, there is a drop in the first minute from about 2.0 to 0.25 g/L, followed by slow leveling off to about 0.05 g/L after about 20–30 min. To explore the effect of pH, we carried out the dropwise addition with pulp suspension at initial pHs of 8 and 2. Despite the quite different pH profiles (Fig. 2) and chlorine profiles (Fig. 3) and the different modes of addition, similar delignification (kappa number) and pulp viscosities were obtained (Table III). Compared to conventional chlorination, the dropwise addition to pulp at pH 2 resulted in a pulp with somewhat higher viscosity. In contrast, the formation of chloro-organics was greatly influenced by the process changes. The AOX formation per unit lignin (kappa number) removed was reduced by about 50% by changing the mode from one charge to dropwise addition.

Further experiments (dropwise addition) were conducted with unbleached kraft pulp using 100% chlorine and using 50% chlorine dioxide substitution (C50 D50) at chlorine factors of 0.15 and 0.25. The kappa numbers and AOX values obtained were compared with those obtained from conventional chlorination using 100% chlorine and using 50% chlorine dioxide substitution (**Tables IV**).

Dropwise addition resulted in a substantial reduction in the formation of chloro-organics (AOX). The amount of AOX substances formed in one-charge bleaching of a (C50 D50) mixture was about the same as that formed in continuous chlorination using 100% chlorine. With dropwise addition of a (C50 D50) mixture, AOX could be reduced by 70–75%, compared to chlorination using 100% chlorine by conventional, one-charge addition. The changes in the yield of selected chlorinated phenols are shown in **Table V**. Dropwise addition resulted in a substantial reduction of these compounds.

IV. Chlorination of unbleached kraft pulp at chlorine factors of 0.15 and 0.25

Addition method	*Chlorine (as Cl_2), %*	*Initial kappa no.*	*CE kappa no.*	*Δ kappa no.*	*Total[a] AOX, kg/o.d. metric ton*	*AOX/ Δ kappa no.*
			0.15 chlorine factor			
One charge	100	32.6	10.8	21.8	3.1	0.14
Dropwise	100	32.6	11.4	21.2	1.4	0.07
One charge[b]	50	32.6	11.0	21.6	1.8	0.08
Dropwise[b]	50	32.6	12.1	20.5	0.8	0.04
			0.25 chlorine factor			
One charge	100	32.6	4.6	28.0	6.6	0.23
Dropwise	100	32.6	5.6	27.0	3.5	0.12
One charge[b]	50	32.6	5.7	26.9	3.5	0.13
Dropwise[b]	50	32.6	6.8	26.0	1.5	0.06

C stage: 40°C, 1 h, 2.5% consistency.
E stage: 70°C, 10% alkali, 5% consistency.
[a]Combined AOX of C and E stages. [b]50% ClO_2 substitution.

V. Chlorophenols in C-stage effluents from chlorination of unbleached kraft pulp at a chlorine factor of 0.25, in units of g/o.d. metric ton

	100% chlorine		*50% substitution*	
Compound	*One charge*	*Drop-wise*	*One charge*	*Drop-wise*
p-Chlorophenol	...	...	...	...
2,4,6-Trichlorophenol	6.3	3.2	3.0	1.0
2,3,4,6-Tetrachlorophenol	0.7	...	...	...
4-Chloroguaiacol	...	...	...	...
4,5- and 4,6-Dichloroguaiacol	13.1	7.2	6.9	3.5
3,4,5-Trichloroguaiacol	0.5	0.2	...	...
4,5,6-Trichloroguaiacol	2.0	0.7	0.7	0.3
Tetrachloroguaiacol	1.8	0.8	0.7	0.3
mono Chlorocatechol	...	...	...	...
Dichlorocatechol	...	...	...	...
Total	24.4	12.1	11.3	5.1

Ellipses indicate negligible amounts.

Chlorination of oxygen-bleached pulp

Similar bleaching experiments (100% chlorine and 50% chlorine dioxide substitution) were carried out with oxygen-bleached pulp. As a result of the rather low initial kappa number (21.6), we used a chlorine factor of only 0.15. Comparing the results in the upper portion of Table IV for the chlorination of unbleached kraft pulp and the results in **Table VI** for the chlorination of the oxygen-bleached pulp, we see that the kappa number reduction of the oxygen-bleached pulp is lower than that of the unbleached pulp. The reduction in AOX formation achieved by modified bleaching of

VI. Chlorination of oxygen-bleached kraft pulp at a chlorine factor of 0.15

Addition method	Chlorine (as Cl_2), %	Initial kappa no.	CE kappa no.	Δ kappa no.	Total AOX, kg/o.d. metric ton	Total AOX/ Δ kappa no.	CED viscosity, mPa•s
One charge	100	32.6	4.1	17.5	2.35	0.13	18.2
Dropwise	100	32.6	4.8	16.8	1.71	0.10	18.4
One charge*	50	32.6	3.2	18.4	1.42	0.08	18.8
Dropwise*	50	32.6	3.9	17.7	1.05	0.06	18.0

C stage: 40°C, 1 h, 2.5% consistency.
E stage: 70°C, 10% alkali, 5% consistency.
*50% ClO_2 substitution.

VII. Chlorophenols in C-stage effluents from chlorination of oxygen-bleached kraft pulp at a chlorine factor of 0.15, in units of g/o.d. metric ton

Compound	100% chlorine		50% ClO_2 substitution	
	One charge	Dropwise	One charge	Dropwise
p-Chlorophenol	...	0.0	...	0.0
2,4,6-Trichlorophenol	3.1	2.3	2.1	1.5
2,3,4,6-Tetrachlorophenol	...	0.0	0.0	0.0
4-Chloroguaiacol	...	...	...	...
4,5- and 4,6-Dichloroguaiacol	4.7	3.5	3.1	2.3
3,4,5-Trichloroguaiacol	0.2	0.1	...	...
4,5,6-Trichloroguaiacol	0.8	0.6	0.5	0.3
Tetrachloroguaiacol	0.7	...	0.4	...
mono Chlorocatechol	...	0.0	...	0.0
Dichlorocatechol	...	0.0	...	0.0
Total	9.5	6.5	6.1	4.1

Ellipses indicate negligible amounts.

oxygen-bleached pulp is significantly lower (26-27% reduction, Table VI) than the AOX reduction found with unbleached kraft pulp (50% reduction, Table IV, at 0.15 chlorine factor).

Only a 50% reduction in AOX substances was achieved with dropwise addition on oxygen-bleached pulp using a (C50 D50) mixture, as compared to one-charge chlorination with 100% chlorine. In the case of unbleached kraft pulp, a 70% AOX reduction could be obtained. The results demonstrate a somewhat diminished response of oxygen-bleached pulp to continuous addition of chlorine, which is apparently caused by the low content of free phenolic lignin structures.

The rather low content of free phenolic lignin structures is due to oxidative cleavage of aromatic rings that contain free phenolic hydroxyl groups (*15*). **Table VII** shows the yields of the simple chlorinated phenols obtained in this set of experiments. The data are in line with the finding that the oxygen-bleached pulp did not respond as well to modified bleaching as did unbleached kraft pulp.

Chlorination of ethanol-extracted pulp

Extraction of the pulp with ethanol resulted in a moderate drop in kappa number from 32.6 to 30.0 and a yield loss of 0.6%. However, with conventional chlorination for the extracted pulp, we observed a reduction in AOX of over 50%. Chlorination of ethanol-extracted unbleached kraft pulp by dropwise addition gave about a 75% reduction in AOX.

The amount of chloro-organics (expressed in AOX per unit lignin removed) in the chlorination of ethanol extract is about five times higher than the amount formed from the original pulp (**Table VIII**). This finding indicates that the low-molecular-weight material extractable by ethanol contributes substantially to the formation of chloro-organics (AOX). This result is in agreement with the results obtained by Hise and Hintz (*16*), who found that brownstock washing with copious amounts of aqueous ethanol led to drastic reductions in the formation of polychlorinated dibenzodioxins (DBDs) and dibenzofurans (DBFs), including the 2,3,7,8-tetra-substituted congeners.

Table IX lists some representatives of the simple phenols found in black liquor and in the pulp extracts. **Table X** presents the comparison of the yields of selected monomeric chlorinated phenols formed in the course of chlorination (chlorine factor = 0.25) of unbleached kraft pulp, ethanol-extracted pulp, and ethanol extract. The major contribution of low-molecular-weight lignin degradation products (ethanol extractables) to the formation of chloro-organics—in this case to, monomeric chlorophenols—is again demonstrated.

Experimental procedures

Unbleached kraft pulp with a kappa number of 32.6 was prepared in our laboratory. The oxygen-bleached softwood kraft pulp (kappa no. 21.6) was obtained from a mill in the southeast United States. Conventional and

VIII. Chlorination of unbleached kraft pulp, ethanol-extracted pulp, and ethanol extract at chlorine factor of 0.25 (100% chlorine)

Addition method	*Lignin, %*	*Kappa no.*	*CE kappa no.*	*CE Δkappa no.*	*Δ lignin*[a]	*Total AOX, kg/metric ton*	*AOX/ Δ lignin*
			Kraft pulp				
One charge	4.9	32.6	4.6	28.0	4.2	6.6	1.6
Dropwise	4.9	32.6	5.6	25.0	3.8	3.5	0.9
			Ethanol extracted pulp				
One charge	4.5	30.0	5.3	24.7	3.7	2.9	0.8
Dropwise	4.5	30.0	5.9	24.1	3.6	1.7	0.5
			Ethanol extract				
One charge	0.4	...	...	...	0.4[b]	3.1	7.8

[a]Change in lignin = CE change in kappa no. × 0.15.

[b]The lignin content in the extract was determined by subtracting the extracted kraft pulp from the unbleached kraft pulp.

IX. Major monomeric phenols in pulp, black liquor, and phenol extract

Black liquor

Acetoguaiacone
2-methoxyphenol
3-guaiacylpropanol
2-guaiacylethanol
Vanillin
3-(4-hydroxy-3-methoxyphenyl)-2-oxo-propanol
3-(4-hydroxy-3-methoxyphenyl)-3-oxo-propanol
3-(4-hydroxy-3-methoxyphenyl)-propanol
3-(4-hydroxy-3-methoxyphenyl)-3-oxo-2-propanol

Pulp

Acetoguaiacone
Guaiacylacetone
1-Guaiacylethanol
Vanillin
1-guaiacylethanol
3-(4-hydroxy-3-methoxyphenyl)-2-oxo-propanol

Ethanol extract

Acetoguaiacone
Vanillin
Dehydrodiconiferyl alcohol

modified bleaching experiments were carried out at 40°C, for 1 h, to a final consistency of 2.5%. The chlorinations by dropwise addition were carried out in a 3-L glass flask provided with a stirrer using pulp samples of about 30 g (oven-dry). Deionized water was used for all experiments.

The unbleached kraft pulp was extracted (48 h) with ethanol in a Soxhlet extractor to obtain ethanol-extracted unbleached kraft pulp and ethanol extract.

The chlorinated pulps were extracted with 5% alkali at 70°C, 10% consistency, for 1 h. After chlorination, the pulp was filtered, and the filtrate was analyzed for AOX and chlorophenol. The pulp was tested for kappa number and viscosity. Kappa numbers were determined using TAPPI T 236 cm-85. Viscosity measurements were made according to TAPPI T 230 om-89. The chloro-organic content (AOX) was determined by neutron activation.

The neutral, phenolic, and acidic fractions were obtained from the C-stage effluents and black liquor by successive extraction with ether at pH 13, 9, and 2 for 48 h at each pH.

The black liquor, pulp, and C-stage effluent extracts were analyzed for monomeric phenols by gas chromatography (GC) and for chlorophenols by gas chromatography–mass spectrometry (GC–MS).

Summary

Continuous, dropwise addition of chlorine to unbleached kraft pulp substantially reduces the formation of chloro-organics (AOX substances and selected monomeric chlorinated phenols). An oxygen-bleached kraft pulp was found less responsive to modified bleaching than an unbleached kraft pulp. Conventional bleaching of ethanol-extracted pulp showed a 50% reduction in AOX formation, suggesting that low-molecular-weight phenolic compounds retained in the brownstock contribute substantially to the formation of chloro-organics.□

Literature cited

1. The National Dioxin Study, Tiers 3,5,6, and 7, U.S. EPA 440/4-87-003, Office of Water Regulations and Standards, Washington D.C., February 1987.
2. Swanson, S. E., Rappe, C., Malmstrom, J., and Kringstad, K. P., Chemosphere 17(4): 681(1988).
3. McBride, A. C., Amendola, G. A., Blosser, R. O., Whittermore, R. C., *et al.*, U.S. EPA/Paper Industry Cooperative Dioxin Screening Study, EPA-440/1-88-025, 1988.
4. Kringstad, K. P., Abe, Z., de Sousa, F., Swanson, S., *et al.*, 1988 CPPA Environmental Conference Proceedings, CPPA, Montreal, p. 47.
5. Kringstad, K. P., Johnson, L., Kolar, M., de Sousa, F., *et al.*, Tappi J. 72(6): 163(1989).
6. Axegard, P. and Renberg, L., Chemosphere 19(1-6): 661(1989).
7. Axegard, P., TAPPI 1988 International Pulp Bleaching Conference, TAPPI PRESS, Atlanta, p. 69.
8. Liebergott, N., TAPPI 1984 Pulping Conference Proceedings, TAPPI PRESS, Atlanta, p. 359.
9. Hise, R., Tappi J. 72(12): 121(1989).
10. Reeve, D. W., High chlorine dioxide substitution in the first stage of pulp

X. Chlorophenols in C-stage effluents, in units of g/o.d. metric ton

Compound	*Kraft pulp*	*Ethanol extract*	*Ethanol-extracted pulp*	
	One charge	*Drop-wise*	*One charge*	*Drop-wise*
p-Chlorophenol	...	...	...	...
Dichlorophenol	...	...	...	...
2,4,6-Tricholorphenol	6.3	3.1	2.6	1.0
2,3,4,6-Tetrachlorophenol	0.7	1.2	0.5	...
4-Chloroguaiacol	...	...	...	...
4,5- and 4,6-Dichloroguaiacol	13.1	7.0	5.7	2.9
3,4,5-Trichloroguaiacol	0.5	0.3	0.2	...
4,5,6-Trichloroguaiacol	2.0	0.7	1.0	0.6
Tetrachloroguaiacol	1.8	1.0	1.1	0.7
mono Chlorocatechol	...	...	...	...
Dichlorocatechol	...	...	...	...
Total	24.4	13.3	11.1	5.2

Ellipses indicate negligible amounts.

bleaching, Albright and Wilson Americas, Division of Tenneco Canada, Inc., January 1981.
11. Axegard, P., Tappi J. 69(10): 54(1987).
12. Annergren, G. E., Calsson, G., and Norrby, M., 1986 EUCEPA Proceedings, EUCEPA, Helsinki, p. 65.
13. Germgard, U. and Karlsson, R., Nordic Pulp Paper Res. J. 4: 166(1988).
14. Lindstrom, K., Nordin, J., and Osterberg, F., *in* Adv. Identification Anal. Organic Pollutants, Vol. 2 (L. H. Keith, Ed.), 1981, p. 1039.
15. Gellerstedt, G. and Lindfors, E.-L., Tappi 70(6): 119(1978).
16. Hise, R. and Hintz, H., Tappi J. 73(1): 185(1990).

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