The effect of brownstock washing on the formation of chlorinated dioxins and furans during bleaching

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ABSTRACT *Poor brownstock washing led to increased levels of polychlorinated dibenzo-p-dioxins (PCDDs) and furans (PCDFs) in softwood pulps after the chlorination stage and in the final effluent. Additional washing in the laboratory with copious amounts of aqueous ethanol decreased chlorinated dioxins and furans by 80%. These results demonstrate the presence of solvent-extractable precursors for PCDD/Fs associated with this unbleached pulp.*

Based on analyses of the brownstock pulps for dibenzo-p-dioxin (DBD) and dibenzofuran (DBF), material balance calculations suggest there must be other precursors for the chlorinated analogs. Spiking unbleached pulps with higher than normal levels of brownstock and screen room defoamers used in our mills had no significant effect on the formation of chlorinated dioxins and furans after bleaching. Laboratory studies also showed that the use of surfactants during brownstock washing could reduce the levels of PCDD/Fs by as much as 25%.

KEYWORDS
Bleaching
Brownstock
Chlorination
Environmental control
Pulping
Surfactants

Small amounts of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2378-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2378-TCDF) have been detected in pulp mill sludges and effluents (*1–7*). It also has been established that these materials are formed mainly if not exclusively in the chlorination stage of bleaching (*6, 7*).

The effect of improved removal of extractable materials during brownstock washing on the formation of PCDDs and PCDFs was evaluated in mill trials and in laboratory bleaching studies. Possible precursors for PCDD/Fs in the unbleached pulp include the unchlorinated analogs, dibenzofuran (DBF), and dibenzo-*p*-dioxin (DBD), as well as low-molecular-weight lignin fragments generated during pulping, which include diaryl ethers, substituted phenols, and catechols. Alkyl-substituted DBD/Fs may be present as well.

Direct chlorination of DBD/F is known to produce PCDD/Fs (*8–15*). The unchlorinated compounds have been detected recently in unbleached and bleached pulps (*9–12*). Brownstock defoamers have been identified as one source of these compounds (*11, 12*). There is still some confusion concerning the relative contribution of these unchlorinated precursors to the overall formation of PCDD/Fs in pulp bleaching.

Published studies with model compounds generally conclude that the chlorination of DBF does produce the TCDF isomers normally associated with pulp bleaching processes (*10–15*). In contrast, early reports suggested that chlorination of DBD did not produce TCDD isomers in a pattern characteristic of bleached pulps (*10, 13, 14*).

When DBD was chlorinated in aqueous solutions, the two major

TCDD isomers were 2378-TCDD and 1278-TCDD, in a ratio of about 60:40 (*10, 14*). Bleaching of pulp in the laboratory typically produced only the 2378-TCDD isomer with only small amounts of the 1278-TCDD isomer (*10, 13, 14*). It was shown in more recent studies that the chlorination of DBD in the presence of bleached pulp does lead to the pattern of TCDD isomers expected in pulp (*15*).

We have consistently found significant levels of the 1278-TCDD isomer in analyses of our laboratory and mill-bleached pulps and also in the chlorination of isolated kraft lignin (**Fig. 1**) (*16*). We have demonstrated that these isomer patterns are strongly affected by the amount of chlorine used for bleaching and reaction time (*17*). The low levels of 1278-TCDD found in some analyses also may be due to a selective loss of certain isomers in the extensive clean-up procedures used (*18*). Artifacts of the analytical procedure can obviously be misleading in developing mechanistic interpretations.

The chlorine substitution pattern also could be influenced by substituents already present on the unchlorinated structure. The existence of alkyl-substituted furans (*19*) and phenoxy-substituted dioxins (*20*) has been reported recently.

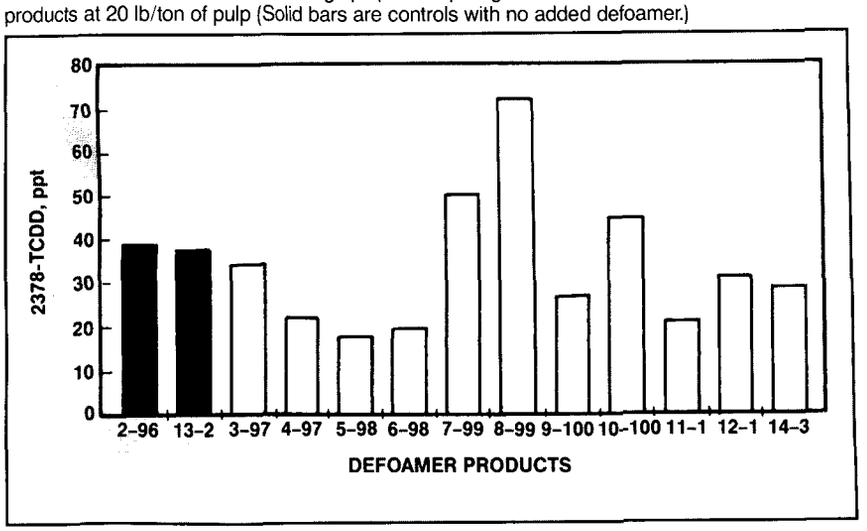
Role of contaminants

The role of contaminants in the formation of PCDD/Fs has been questioned since the discovery of chlorinated dioxins and furans in pulp mill effluents and sludges. Numerous organic and inorganic additives are used in every part of the papermaking process. Swedish researchers have presented evidence that evaporator condensates from the process of concentrating black liquor can enhance the formation of PCDD/Fs in C-stage pulps (*19*). A common energy-saving and water-conserving practice is to use the hot condensate as shower water on the final stage of the brownstock washers. The carry-over of black liquor solids into the bleach plant due to incomplete washing also may enhance the formation of PCDD/Fs.

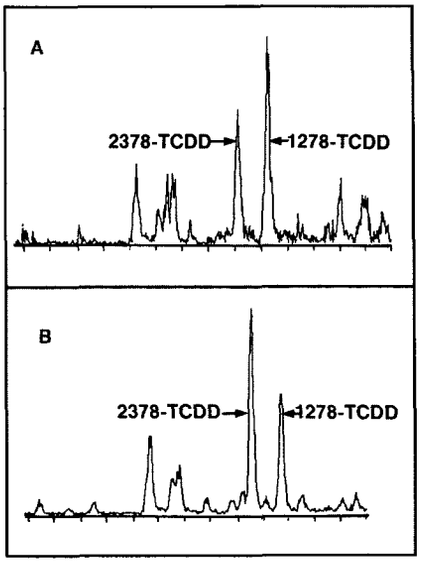
Canadian studies showed that some oil-based additives used in brownstock washing and other areas to control the natural foaming tendencies of pulp mill filtrates contained relatively high levels of DBF (*11, 12*). When these products were added to unbleached pulp in the laboratory at three to five times the normal application rate, a dramatic enhancement of both 2378-TCDD and 2378-TCDF levels in chlorinated pulp was observed in several cases (**Table I**).

After reviewing their work, we conducted similar tests on 12 commercial defoamer products used in our mills and found that none of the products tested gave such dramatic increases in TCDD/F levels (**Fig. 2**). Those products which gave levels of 2378-TCDD slightly higher than the controls (no added defoamer) are no longer used in our mills. Several defoamer suppliers are actively working with their oil suppliers to ensure that only the highest quality oils are used in their formulations.

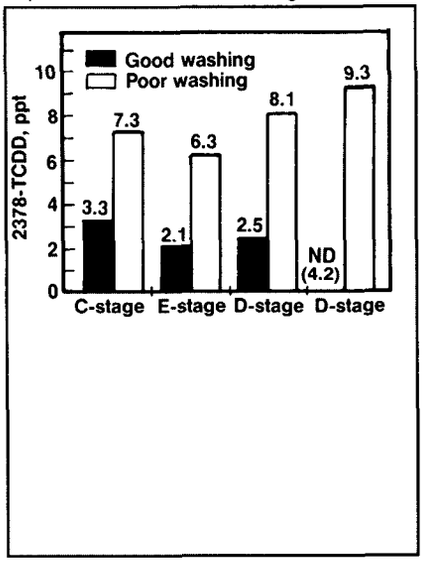
2. Formation of 2378-TCDD in C-stage pulp after spiking brownstock with commercial defoamer products at 20 lb/ton of pulp (Solid bars are controls with no added defoamer.)



1. TCDD isomers on chlorination of (A) unbleached softwood pulp and (B) isolated softwood lignin



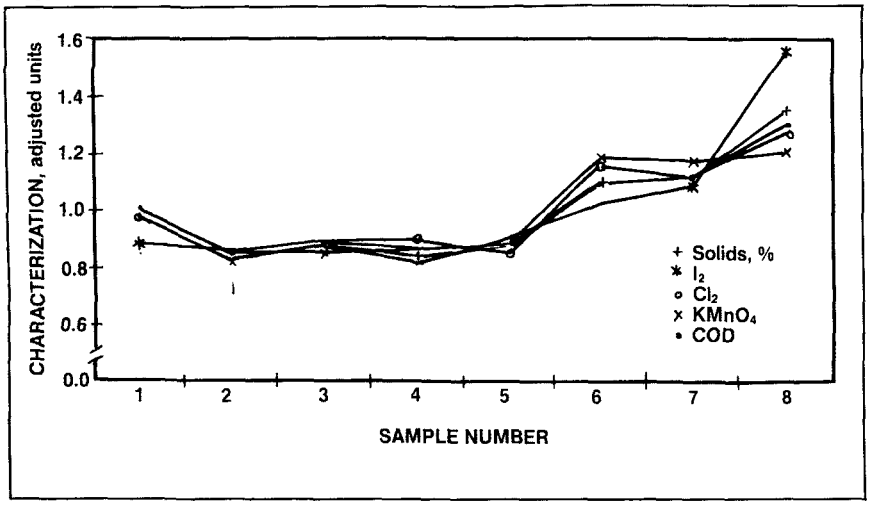
3. The effect of brownstock washing on the formation of 2378-TCDD in mill-produced hardwood pulps. D-stage samples were duplicates from the same D-stage



Effect of brownstock washing

Trials were conducted in 1987 at a Westvaco mill to test the effects of black liquor carry-over. Brownstock washing was improved for a 30-h period by increasing the shower water flow and maintaining relatively low production rates. A second 24-30-h

4. Characterization of liquid squeezed from brownstock pulp during poor washing trial, third-stage brownstock washer



degree of washing during the trials (**Fig. 5**). The carry-over was about 30% higher in the pulp from the final wash stage during the poor washing period. After screening, the difference in the carry-over between the two trial periods was slightly less, requiring from 10–20% more permanganate.

The average permanganate consumption of the liquid associated with the screened pulp was 1.7 g/L during the poor washing trial versus 1.5 g/L during the period of good washing. A 1.5-g/L permanganate consumption corresponds roughly to a chlorine demand of about 0.3 g/L. Chlorination of the material in this liquid can require as much as 10 lb Cl_2/ton of pulp, depending on the water recycle pattern at the mill.

I. Effect of added defoamers or oil on formation of 2378-TCDD/F during the chlorination stage (*12*)

	2378-TCDD, ppt	2378-TCDF, ppt
Control	11	160
Defoamer A	110	910
Defoamer B	81	280
Defoamer C	140	1200
Base oil from C	170	1400

trial was conducted later in the same week with decreased shower water flow to simulate relatively poor brownstock washing. Composite samples were taken throughout the bleach plant and waste treatment system to characterize each period. These were analyzed for TCDD/Fs. The results are shown graphically in **Fig. 3**. The chlorinated and extracted pulps and final bleached pulp all had lower TCDD/F levels during the period of good washing.

Characterizing brownstock washing

The efficiency of brownstock washing stages in removing solids from pulp is commonly used as a measure of washing performance. This performance can be determined by measuring sodium carry-over for instance and is often expressed as Na_2SO_4 (salt cake) loss. In our study, the quantity of organic material carried into the bleach plant with the brownstock was considered to be more important. Therefore, several tests were used to determine organic carryover more directly.

The liquid squeezed from the brownstock pulp was subjected to a variety of tests to quantify the amount of chlorine-reactive organic material present. Tests included chlorine demand, chemical oxygen demand (COD), permanganate demand, and iodine demand. The percent solids in the liquid was determined also for comparison. Pulp samples were taken from the last stage of the brownstock washers and from the deckers, which thicken the pulp after screening. As shown in **Fig. 4**, all these tests gave similar information. The y-axis values were normalized to facilitate comparison of these techniques. Samples were collected every 3 h during the "poor washing" phase of the mill trial. The permanganate consumption test was chosen for further work since the test is easily run and the chemicals used are familiar and readily available at the mills.

This test was used to quantify the

Ethanol washing of brownstock

The limits of improved washing were tested in the laboratory by washing a brownstock pulp sample with both aqueous and absolute ethanol before chlorination. As compared to no washing, the solvent washing lowered the amount of 2378-TCDD/F formed in the subsequent stage by up to 80% (**Figs. 6 and 7**). Based on precursor analyses, this solvent washing did not remove all of the unchlorinated DBD and DBF from the unbleached pulp, but a substantial reduction was obtained (**Table II**).

It appears likely that other precursors for PCDD/Fs exist. The ethanol-washed brownstock contained only 7.2 ppt of DBD, or about 40 "femtomoles" per gram of pulp (fm/g). The C-stage pulp alone contained 20.7 ppt (65 fm/g) of 2378-TCDD and 61 ppt (190 fm/g) of all TCDD isomers. Some TCDDs were probably present in the filtrate, although it was not analyzed. Furthermore, the 40 fm/g of DBD would have been converted to penta-, hexa-, hepta-, and octachloro isomers as well as tetrachloro.

For the furans, the ethanol-washed pulp contained 1540 ppt of DBF, or about 9.2 picomoles per gram of pulp (pm/g). According to Canadian results, the conversion of DBF to 2378-TCDF is about 0.94 mole percent (*15*). We found that about eight times more 2378-TCDF was produced in the C-stage pulp alone than would be predicted by using this conversion factor.

Since more chlorinated dioxins and

furans were formed than can be explained by the residual DBD or DBF in the ethanol-washed pulp, we propose that degradation of residual lignin during bleaching leads to formation of PCDDs.

The effect of treating the brownstock pulp with an extended leaching at high pH and then water washing before chlorination also was tested in the laboratory. The purpose was to test a more practical means to further promote the removal of low-molecular-weight lignin and other precursors before chlorination. A 3-h leaching period at pH>11 lowered the 2378-TCDD levels by 25% and the 2378-TCDF level by over 60%, as compared to bleaching an untreated brownstock pulp. Since the leaching lowered the kappa number, the chlorine charge was reduced to maintain a constant chlorine factor (CF), as defined here: CF = % Cl_2/kappa number. The sum of all tetrachloro-substituted dioxins was reduced by about 60% as a result of the extended leaching period.

Washing with surfactants

Another more practical way to improve brownstock washing was tested in the laboratory. Several experimental surfactants which were being developed as "drainage aids" were used in laboratory simulations to test the effect of improved washing on the formation of TCDD/Fs.

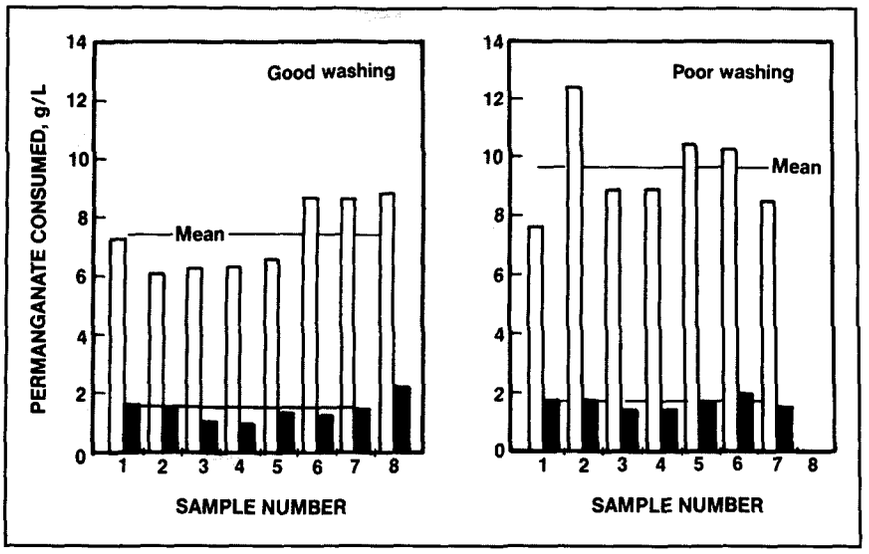
As shown in **Table III**, two of the additives were effective in lowering the 2378-TCDD levels in C-stage pulps about 20%, as compared to a control in which the brownstock was washed with water only. Filtrates were not analyzed. The levels of 2378-TCDF also were lowered by about 20–25%.

These results suggest that employing drainage aids in brownstock washers could be used to lower the levels of PCDD/Fs formed in bleaching. However, the effect was relatively small as compared to other process options being developed.

Conclusions

The effectiveness of brownstock washing influences the concentrations of PCDD/Fs formed in the first stage of bleaching. Poor washing in mill trials produced higher levels of these materials than during a control period with good washing. Removing extractable material from unbleached pulp in the laboratory with ethanol resulted in significantly lower concentrations of TCDD/Fs upon bleaching. Based on the quantity of unchlorinated dioxins and furans remaining in the ethanol washed pulp, other precursors for TCDD/Fs must exist. Residual lignin remaining undegraded in the fiber is proposed as a source of these materials. The use of experimental drainage aid in laboratory simulations of brownstock washing (surfactants) lowered the formation of TCDD/Fs by 20–25%.

5. Permanganate consumption of liquid squeezed from brownstock pulp during mill trials. Solid bars are samples from deckers after screening. Open bars are samples from the final stage of brownstock washing.



III. Effect of washing aids (surfactants) in brownstock washing on formation of TCDD/Fs in C-stage softwood pulps; CF = 0.27

	2378-TCDD, ppt	*Total TCDD, ppt*	*2378-TCDF, ppt*	*Total TCDF, ppt*
Control	33.1	33.1	488	1153
Product 1	33.8	33.8	452	1184
Product 2	26.6	29.8	359	831
Product 3	25.7	33.1	331	862

II. Effect of ethanol washing on removal of dibenzo-*p*-dioxin (DBD) and dibenzofuran (DBF) from softwood brownstock pulp

Sample description	*DBD, ppt*	*DBF, ppt*
Control		
Unbleached pulp	189	5600
C-stage pulp	60	4590
E-stage pulp	22	2700
EtOH Washed		
Unbleached pulp	7.2	1540
C-stage pulp	4.5	3940
E-stage pulp	8.9	2320

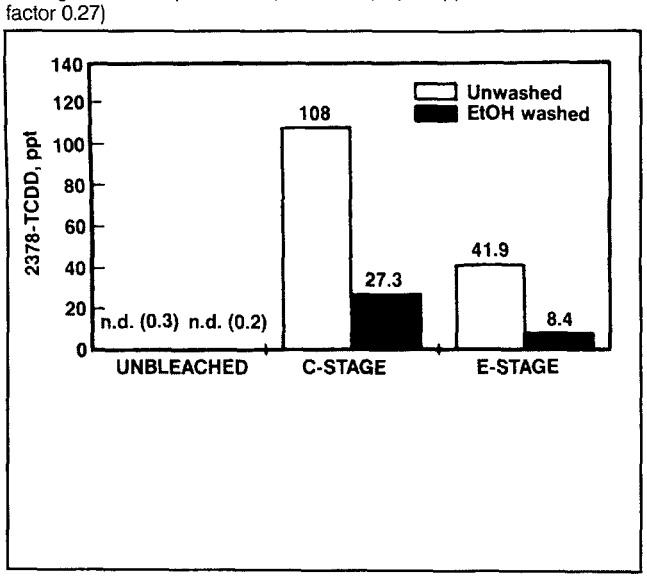
Experimental procedures

General methods

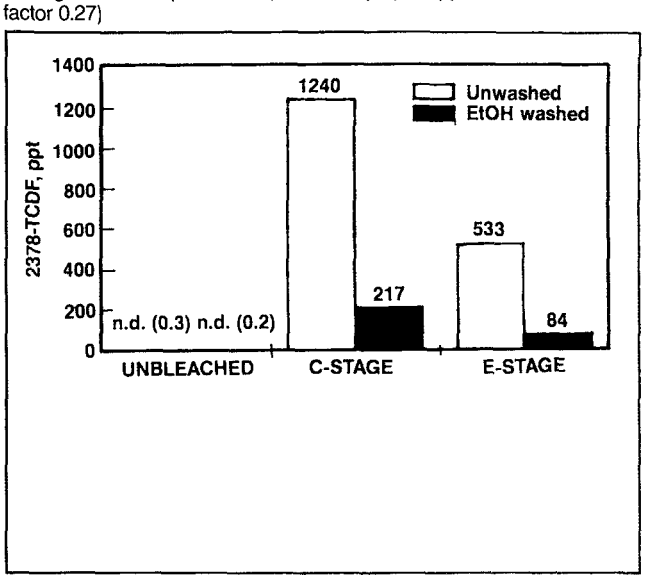
Unbleached, screened softwood pulp was collected from a mill. The kappa number was determined using TAPPI um T236 os-76. An aliquot of the pulp was processed through the chlorination and extraction stages with no additional prewashing or processing. Another aliquot of pulp was extensively washed with water, aqueous ethanol, and then absolute ethanol (described in a later section) before bleaching.

The kappa factor *KF* is defined as

6. The effect of ethanol washing on the formation of 2378-TCDD; average of two experiments (softwood pulp, kappa no. 26.4, chlorine factor 0.27)



7. The effect of ethanol washing on the formation of 2378-TCDF; average of two experiments (softwood pulp, kappa no. 26.4, chlorine factor 0.27)



IV. Experimental conditions for laboratory work

	Set 1		*Set 2*	
	Un-washed	*EtOH washed*	*Un-washed*	*EtOH washed*
Before chlorination				
Kappa number	26.4	26.4	26.4	26.4
Viscosity, cp	27.1	27.3	27.1	27.3
Chlorination				
O.d. pulp used, g	70	70	300	290
Final pH	1.4	1.4	1.6	1.6
Actual Cl_2 consumption, % on o.d. pulp	7.9	7.9	7.9	7.9
25 mL K number	6.7	7.9	6.4	6.3
Extraction				
O.D. pulp used, g	40	40	60	60
Alkali, %	3.0	3.0	3.0	3.0
Initial pH	11.7	11.9	12.5	12.9
Final pH	8.1	8.5	9.8	9.5
25 mL K number	3.6	3.9	3.4	3.4

$$KF = [\%\ Cl_2 + (\%\ ClO_2 \times 2.63)]/\text{kappa number}$$

A *KF* of 0.30 was used in all chlorinations with 10% substitution of ClO_2, added after Cl_2-water. The unbleached pulp kappa number did not change after ethanol washing as compared to the original pulp. After chlorination, the pulp slurry was thickened with no additional washing to maximize PCDD/F concentrations in the pulp. High chlorine charges were used to ensure the formation of measurable levels of PCDD/Fs.

Experimental details are given in **Table IV.**

Filtrate permanganate consumption

The liquid squeezed from unbleached pulp samples was subjected to essentially a K number, or permanganate number, test using 25 mL. The volume of filtrate used in the test was adjusted to give near 50% consumption of the permanganate. Total liquid volume was adjusted to 200 mL. Acid and permanganate were added to the stirred liquid and were allowed to react for 10 min. A potassium iodide solution was added to quench the unreacted permanganate, and the iodine was titrated with standardized sodium thiosulfate.

Ethanol washing. The desired quantity of unbleached softwood pulp was slurried in water at 1% consistency and was stirred mechanically for 10 min.

The slurry was filtered using a 300-mesh screen in a large Buchner funnel. (Contact with plastics and paper were avoided — all glassware was rinsed before use with absolute ethanol). The "first pass" filtrate was poured back through the formed pad of pulp to retain fines and fibers. As much filtrate was removed as possible using aspirator vacuum.

The pulp was then washed (without disrupting the pad) with a volume of 50% aqueous ethanol equivalent to three times the estimated water con-

tent of the pad. The ethanol was added without vacuum on the Buchner funnel, was allowed to sit 1 min, and was then pulled through the pad by suction. No fines loss was noted by visual inspection of the lightly colored filtrate. This washing was repeated with warm (45°C) absolute (200 proof) ethanol, then again with 50% aqueous ethanol, and finally with portions of hot deionized water until the ethanol odor in the pulp was not detectable.

The pad was mixed in a Hobart mixer. Pulp kappa number was found to be unchanged as compared to the unwashed sample. Yield was near 96% after ethanol washing.

Chlorination stage. Seventy- or 300-gram batches (o.d. basis) of pulp at 3% consistency were chlorinated in 2-L or 12-L continuously stirred reactors. Chlorination temperature was 50°C, and retention time was 1 h in every case. All tests were conducted at 10% substitution of ClO_2, added 15 s after injection of chlorine water. Residual active chlorine in the filtrate was determined following the reaction. Chlorinated K numbers (25 mL) were determined as well. See Table IV for additional experimental details.

Extraction stage. Forty- or sixty-gram batches of pulp were extracted at 70°C in a stainless steel Parr reactor for 1 h. Testing on this pulp included viscosity and CE K number.

Analytical. Aliquots of unbleached, chlorinated, and extracted pulps were analyzed for PCDD/F and DBD/F by Triangle Laboratories, Inc.□

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