# Pretreatment and posttreatment of pulps to eliminate dioxins

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*ABSTRACT: Nitrogen dioxide treatment of dibenzo–p–dioxin and dibenzofuran spiked cotton linters effectively reduced polychlorinated dibenzo–p–dioxin and dibenzofuran levels after chlorination of the linters. A similarly spiked wet pulp gave extremely low levels of dioxin compounds when pretreated with ozone before chlorination; a nitrogen dioxide pretreatment followed by chlorination gave a modest dioxin reduction. Posttreatments of dioxin-containing pulps with ozone, hydrogen peroxide, and oxygen led to about 50% reductions in dioxin.*

*KEYWORDS: Dioxins, furans, nitrogen compounds, nitrogen dioxide, nitrogen oxides, oxides, oxygen heterocycles, ozone, pretreatment, pulps.*

Previous studies have indicated that dibenzo-p–dioxin (DBD) and dibenzofuran (DBF) are important precursors to the production of polychlorinated dibenzo–p–dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) when bleaching wood pulp with high levels of chlorine.[1] **Figure 1** shows the structures of DBD and DBF as well as 2,3,7,8–tetrachlorodibenzo–p–dioxin (2378–TCDD) and 2,3,7,8–tetrachlorodibenzofuran (2378–TCDF).

Our purpose in this paper was to answer the question whether it was possible to destroy DBD and DBF components selectively before chlorine bleaching. This would thereby reduce or eliminate PCDD and PCDF. To answer this question, we first conducted an extensive study of the reactions of DBD and DBF spiked cotton linters with nitrogen dioxide, nitric acid, sulfuric acid, oxygen, hydrogen peroxide, and ozone to determine what type of reagents would react with DBD and DBF.[2] We chose these reagents for their low cost and possible commercial potential. Since nitrogen dioxide and ozone offered the best performance, we selected them for further testing. We further selected ozone for studies to define the reactivity differences of DBD and DBF with the lignin in pulp.[3]

While ozone and nitrogen dioxide reacted well with the PCDD and PCDF precursors, their use in pulp treatment may still not prevent PCDD and PCDF formation upon chlorination for two reasons:

- The lignin in the pulp consumes all the reagent.
- The alteration of the precursor by the reagent may not be permanent.

As an example, consider nitrogen dioxide selectively attacking DBD and DBF to give a nitrogen dioxide substituted product with chlorine replacing the nitrogen dioxide group during chlorination. It was, therefore, imperative that we conduct chlorinations of samples containing DBD and DBF that had first undergone treatment with ozone and nitrogen dioxide. We describe the results of these experiments in this paper.

Our strategy was to test first the efficacy of pretreatment with DBD and DBF spiked cotton linters. Spiking

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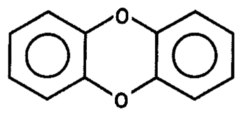
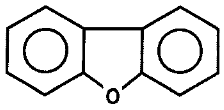
[2]Sonnenberg, L. B. and Dimmel, D. R., *Envir. Sci. Tech.* 27(7): 1334(1993).

[3]Sonnenberg, L. B. and Dimmel, D. R., *J. Wood Chem. Tech.*, in press.

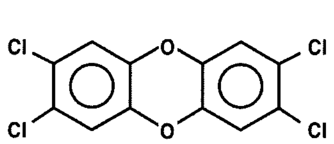
1. Chemical structures for DBD, DBF, 2378–TCDD, and 2378–TCDF



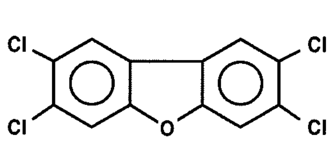
DBD



DBF



2378-TCDD



2378-TCDF

I. Results for cotton linters pretreatment samples

| | Unreacted, chlorinated | Ozone reacted, chlorinated | Nitrogen dioxide reacted, chlorinated | Process blank | Ozone-reacted, non-chlorinated | Nitrogen dioxide-reacted, non-chlorinated |
|---|---|---|---|---|---|---|
| Analyte concentration, ng/g of linter | | | | | | |
| DBF | 5.0 | 5.0 | 3.7 | 15 | 27 | 7.6 |
| DBD | 0.28 | 0.071 | 0.010 | 0.10 | 12 | 0.050 |
| Mono-CDF | 0.088 | 0.041 | 0.026 | 0.031 | ND | ND |
| Mono-CDD | 0.053 | 0.014 | ND | ND | ND | ND |
| Di-CDF | 7.9 | 5.0 | 3.1 | ND | ND | ND |
| Di-CDD | 0.20 | 0.057 | ND | ND | ND | ND |
| Tri-CDF | 17 | 17 | 5.8 | ND | 0.02 | ND |
| Tri-CDD | 6.4 | 1.6 | 0.013 | ND | 0.01 | ND |
| Tetra-CDF | 2.7 | 4.3 | 0.98 | ND | ND | ND |
| Tetra-CDD | 18 | 7.5 | 0.041 | ND | 0.05 | ND |
| Internal standard recoveries, % | | | | | | |
| DBF – $^{13}C_{12}$ | 65 | 52 | 65 | 36 | 31 | 59 |
| DBF – $^{13}C_{12}$ | 63 | 60 | 64 | 47 | 28 | 58 |
| TCDF – $^{13}C_{12}$ | 46 | 52 | 61 | 43 | 41 | 59 |
| TCDD – $^{13}C_{12}$ | 48 | 50 | 57 | 40 | 40 | 58 |

greatly simplifies analysis and provides improved accuracy. We then repeated the pretreatments with unbleached pulps to demonstrate their effectiveness in lowering PCDD and PCDF levels in the presence of lignin.

A second area of study was to examine procedures for reducing PCDD and PCDF levels in pulps. We treated a bleached pulp containing trace levels of PCDD and PCDF with ozone, hydrogen peroxide, oxygen, and other possible commercial electrophilic reagents. This would determine the stability of PCDD and PCDF to various post–chlorine bleaching stages.

II. Results for pretreated pulp samples

| | Ozonated, chlorinated pulp | | Nitrogen dioxide treated, chlorinated pulp | | Spiked pulp control | Laboratory method blank |
|---|---|---|---|---|---|---|
| | Values | Average | Values | Average | Values | Values |
| Concentration, pg/g | | | | | | |
| 2378–TCDF | 3.0, 3.0 | 3.0 | 399, 409 | 404 | ND, ND | ND |
| Total TCDF | 4.9, 3.0 | 4.0 | 590, 606 | 598 | | |
| 2378–TCDD | ND, ND | ND | ND, 3.0 | 1.5 | ND, ND | ND |
| Total TCDD | ND, ND | ND | ND, 3.0 | 1.5 | ND, ND | ND |
| Recoveries, % | | | | | | |
| 2378–TCDD-$^{13}C_{12}$ | 69, 66 | | 62, 64 | | 86, 84 | 86 |
| 2378–TCDF-$^{13}C_{12}$ | 62, 56 | | 54, 53 | | 72, 80 | 70 |
| 2378–TCDD-$^{37}Cl_{14}$ | 98, 89 | | 95, 95 | | 97, 99 | 93 |

## Results

### Effects of pretreatments on spiked cotton linters

Our chlorinated samples of $NO_2$-treated and $O_3$-treated DBD and DBF spiked cotton linters produced the data presented in **Table I.** The values in the table are an average of duplicate results. In addition to values for DBF and DBD, there were also measurements for several chlorinated derivatives. The derivatives ranged from one to four (mono to tetra) chlorine substitutions for each set. Not detected (ND) in the table indicates a lack of detection of the analyte above the estimated method detection limit of 0.005 ng/g.

The spike levels before nitrogen dioxide treatment were 19 ppb DBF and 17 ppb DBD. The nitrogen dioxide treatment of spiked cotton linters is

**III.** TCDD and TCDF levels on a wet basis for posttreatment of chlorinated pulp samples

| | Concentration, pg/g | | | | |
|---|---|---|---|---|---|
| Sample | Total TCDF | 2378–TCDF | Total TCDD | 2378–TCDD | Moisture, % |
| Untreated E stage | 84 | 52 | 1.1 | 0.5 | 81 |
| Untreated E stage | 81 | 51 | 2.4 | 1.1 | |
| Ozone and sodium hydroxide treated | 3.3 | 2.1 | ND | ND | 85 |
| Ozone and sodium hydroxide treated | 6.0 | 4.6 | ND | ND | |
| Ozone treated | 45 | 28 | ND | ND | 79 |
| Ozone treated | 42 | 26 | ND | ND | |
| Hydrogen peroxide treated | 32 | 20 | ND | ND | 79 |
| Hydrogen peroxide treated | 45 | 27 | ND | ND | |
| Method blank | ND | ND | ND | ND | |

known to reduce DBD levels almost completely and DBF by one third.[2] The present analysis showed a similar trend—nearly complete loss of DBD and partial loss of DBF. In addition, there are substantially lower PCDD and PCDF levels especially of the tetrachlorodibenzo–p–dioxin (TCDD) type. The DBD and DBF which the nitrogen dioxide treatments destroy apparently do not revert to chlorinated DBD and DBF products upon chlorination.

Columns 5 and 6 of Table I show that the degradation of cotton linters by ozone was much less than by nitrogen dioxide. Comparing columns 2 and 3 of Table I shows that there are more chlorinated products after chlorination. We prepared the spiked DBD and DBF linters used in the ozone experiment in a similar manner to that of the nitrogen dioxide experiment. There was insufficient sample, however, to confirm the exact loading levels. Quite obviously, the ozone treatment was not very effective. Yet, previous work established that ozone efficiently destroyed DBD and DBF spiked on linters.[2]

There was a very important difference in the two ozone treatments. The earlier, effective treatments used wet linters, and the present, ineffective treatment used dry linters. We therefore reexamined the effectiveness of ozone with pulp. For this sample set, internal standard recoveries were generally acceptable at greater than 40%. The analytical precision was also good with 30–50% agreement for most duplicates.

## Effects of pretreatment on pulp

We treated a pulp spiked with 0.2 ppb DBD and 10 ppb DBF with ozone in one case and nitrogen dioxide in another case. Then we chlorinated the treated pulps. We employed common, commercial practices and based the level of chlorine on the residual lignin remaining in the pulp. **Table II** shows the results.

There was good precision between duplicate samples. Internal standard and cleanup standard recoveries were greater than 50% in all cases, indicating efficient removal of TCDD and tetrachlorodibenzo–p–furan (TCDF) from the sample matrix.

The data in the table indicate that ozone treatment is very effective in producing a pulp with low TCDD and TCDF levels. One should compare the values observed for TCDF and TCDD (4 and nondetectable, respectively) to the levels of TCDD and TCDF expected from a chlorinated, nonalkali extracted DBD and DBF spiked pulp without pretreatment. We did not analyze such a pulp but estimate it to be greater than 3600 parts per thousand TCDF and greater than 22 parts per thousand TCDD. This estimate comes from TCDD and TCDF analyses of the combined pulp and aqueous phases from the oxygen and alkali treatment of spiked chlorinated pulp (see Table V). To the extent that the oxygen treatment destroyed TCDD and TCDF, the values present in the untreated pulp will be greater than those observed after treatment. Part of the TCDD and TCDF lowering observed with ozone treatment may relate to the lower level of chlorine employed with this pulp which contained less residual lignin.

The nitrogen dioxide pretreatment was effective at lowering TCDD and TCDF levels, but it was not nearly as effective as ozone. The observed levels of 600 parts per thousand TCDF and 1.5 parts per thousand TCDD were still well below the levels which could arise from a pulp spiked with 10,000 parts per thousand DBF and 200 parts per thousand DBD.

## Posttreatment of pulps containing dioxins

We chlorinated and extracted with base the DBD and DBF spiked pulp described above. We then treated the resulting pulp which should contain enriched levels of PCDD and PCDF with three oxygen-based bleaching systems: oxygen and sodium hydroxide, hydrogen peroxide, and ozone. We analyzed the chlorinated pulp and treated pulps for TCDD and TCDF to determine if commercial electrophilic reagents were capable of destroying these compounds. **Table III** presents the results. In this table, ND indicates analyte undetected above the estimated detection limit of 0.8 parts per thousand.

The untreated E–stage pulp had a TCDF concentration of approximately 83 parts per thousand. This relatively low value probably means that significant amounts of TCDF partitioned from the pulp to the E-stage extract. The spiked pulp began with 10,000 parts per thousand DBF. The TCDF concentration in the oxygen and sodium hydroxide treated pulp decreased by approximately 95%. The reduction in the hydrogen peroxide and ozone cases was about 50%. The concentration of TCDD in the untreated E-stage pulp was approximately 2 parts per thousand. TCDD was not present in any of the treated pulps at levels above the analytical detection limit of 0.8 parts per thousand. In all samples, the 2378–TCDD and 2378–TCDF isomers were the major contributors to the total TCDD and TCDF concentrations. There were five additional isomers of TCDF but only one additional isomer for TCDD.

There were no tetrachlorodioxins and furans in the method blank processed with these pulp samples indicating that the samples did not undergo any contamination during sample preparation and analysis. **Table IV** presents internal standard recoveries for these analyses. Recoveries were 79% or greater which indicates efficient extraction of TCDF and TCDD from the pulp matrix and minimal loss of TCDF and TCDD through extract cleanup procedures. Most du-

**IV.** Internal standard recoveries, %, for posttreated chlorinated pulp samples

| *Sample* | *TCDF – $^{13}C_{12}$* | *TCDD – $^{13}C_{12}$* |
|---|---|---|
| Untreated E stage | 102 | 108 |
| Untreated E stage | 79 | 85 |
| Ozone and sodium hydroxide treated | 92 | 97 |
| Ozone and sodium hydroxide treated | 98 | 101 |
| Ozone treated | 113 | 127 |
| Ozone treated | 110 | 111 |
| Hydrogen peroxide treated | 95 | 105 |
| Hydrogen peroxide treated | 88 | 86 |
| Method blank | 122 | 139 |

## Experimental

In conducting chlorinations of DBD and DBF compounds, one must take extreme care, since highly toxic PCDD and PCDF products may result. One should only attempt experiments with PCDD and PCDF compounds after a thorough review of safe handling and product disposal procedures for such compounds.

### Ozone treatment of spiked cotton linters

We prepared a blank by adding 50 mL of $CH_2Cl_2$ to 5 g of the linters in a 1-L round bottom flask. We evaporated the mixture to apparent dryness on a rotary evaporator. We rotated the flask while introducing a stream of nitrogen containing ozone. The amount of ozone corresponded to 2% of the weight of the pulp. After addition of the ozone, we purged the flask for a few minutes with nitrogen to remove the excess ozone. We then placed the treated linters in an acid–washed, solvent–rinsed jar.

We placed approximately 23 g of cotton linters and 200 mL of $CH_2Cl_2$ containing a fresh dose of 1.4 μL of approximately 1 μg/μL stock solution of DBD and DBF in hexane into a 2000-mL round bottom flask. We stoppered and shook the flask. The slurry sat for 2 h with frequent shaking. We evaporated the linters to apparent dryness on a rotary evaporator and tightly stoppered the flask. We did not conduct confirmation of spike levels by gas chromatographic analysis, since there was insufficient sample available. Typically one loses half of the spike in this procedure. We ozonated approximately 15 g of spiked linters with a 2% charge and handled this similarly to the blank sample.

### Nitrogen dioxide treatment of spiked cotton linters

We spiked the extracted, dry cotton linters as above with approximately 60 ppb of DBD and DBF. Actual spike levels after solvent evaporation were 19 ppb of DBF and 17 ppb of DBD for linters using gas chromatographic analysis. We used dry linters to optimize the reaction, since water will react competitively with nitrogen dioxide. We placed the dry, spiked linters in a flask and subjected it to approximately 25 in. Hg vacuum. We placed approximately 0.2 g of cold nitrogen dioxide in a

**V.** TCDD and TCDF levels on a wet basis of repeat experiment for posttreatment of chlorinated pulp with oxygen and sodium hydroxide

| | *Chlorinated, oxygenated pulp* | | | *Laboratory method blank* |
|---|---|---|---|---|
| | *Values* | *Average* | *Effluent* | |
| Concentration, pg/g | | | | |
| 2378–TCDF | 28, 34 | 31 | 2400 | ND |
| Total TCDF | 40, 49 | 45 | 3600 | ND |
| 2378–TCDD | ND, ND | ND | 22 | ND |
| Total TCDD | ND, ND | ND | 22 | ND |
| Recoveries, % | | | | |
| 2378–TCDD-$^{13}C_{12}$ | 73, 71 | | 6.4 | 86 |
| 2378–TCDF-$^{13}C_{12}$ | 63, 59 | | 9.3 | 70 |
| 2378–TCDD-$^{37}Cl_{14}$ | 92, 86 | | 100 | 93 |

plicate results were relatively consistent indicating acceptable analytical precision.

The results were surprising in that the oxygen treatment appeared to be so much better than ozone. We therefore repeated the oxygen and sodium hydroxide experiment except this time the starting material was a chlorinated, but not alkali extracted, spiked pulp. **Table V** shows these results. The internal standard recoveries for the pulp samples were above 50% indicating efficient removal of the TCDD and TCDF from the pulp matrix. Precision between duplicate results was good. The internal standard recoveries for the effluent sample at 10% were low. Recovery of the cleanup standard was 100%. These results suggest inefficient removal of TCDD and TCDF from the effluent sample before extract cleanup, since analyte losses did not occur in the extract cleanup. We corrected the analyte concentrations for these low recoveries.

The levels in the repeat experiment were about 45 parts per thousand TCDF and nondetectable for TCDD in the pulp as Table V indicates. These values are similar to that previously found for ozone and for hydrogen peroxide. There is a fundamental difference between the level of water present in the ozone, peroxide, and oxygen and sodium hydroxide experiments. For ozone, there was no separation of the reacted pulp from water solvent, since there was no solvent. We conducted the hydrogen peroxide experiments in the presence of 2% sodium hydroxide using 12% pulp in 88% water. At the conclusion of the experiment, we squeezed the treated pulp to remove moisture for the determination of re-

double stopcock pipette connected to a modified rotary evaporator.[2] We expanded the nitrogen dioxide over a 2-min period into the linters by slowly opening two valves in the apparatus and allowing the vacuum to pull most of the nitrogen dioxide into the flask. After 5 min of treatment, we opened the valves to pull in small amounts of air so the remaining nitrogen dioxide would enter the flask and convert any nitrogen oxide present to nitrogen dioxide. After 10 min reaction time at room temperature, we removed the excess nitrogen dioxide by repeated application of vacuum and nitrogen purging. We also subjected the control sample to the vacuum and nitrogen purging sequence.

**Chlorination of spiked cotton linters samples**

We chlorinated three 5-g samples of nitrogen dioxide treated linters, two 5-g samples of ozone treated spiked linters,[2] and two untreated linters samples as before.[1] We did not spike one nitrogen dioxide linters sample. This was the process blank. The method of chlorination, work up, internal standard spiking, concentration through alumina columns, and analysis was identical to that previously described for the other cotton linters reactions.[1]

**Chlorination of nitrogen dioxide treated spiked pulp**

We fluffed the DBD and DBF spiked pulp which was at 30% consistency with nitrogen and 161.4 g (49.5 g o.d. basis) and placed the material in a 5-L round bottom flask attached to a rotary evaporator. We treated the pulp with 1.0 g of nitrogen dioxide employing the procedure mentioned above. After 10 min reaction time, we added 664 mL water to the flask and then shook it for 1 min. We emptied the flask along with 412 mL of rinse water. We stirred the pulp which now was 4% consistency and filtered it under vacuum for 6 h using a nitrogen seal. We chlorinated the whole sample using the same conditions as described for the chlorination of DBD and DBF spiked pulp.[1]

**Chlorination of ozone treated spiked pulp**

We fluffed the DBD and DBF spiked pulp at 31% consistency with nitrogen. We washed 160 g (50 g o.d. basis) with acetic acid to pH 3 and placed it in a round bottom flask attached to a rotary evaporator. We treated the pulp for 12.5 min with an oxygen stream containing ozone. On the basis of the o.d. weight of pulp, we applied 2.1% ozone and consumed 1.8% ozone. The final pH was 3.2, and the final kappa number was 5.9. We performed the chlorination of 40 g of this pulp as described below except with less application of chlorine, since the pulp contained less lignin. The chlorine level was 1.18% with a kappa factor of 0.2. The conditions were 30 min at 45°C with 3% consistency and a final pH of 2.2.

**Chlorination of DBD and DBF spiked pulp**

We slowly dropped a solution of methanol containing small, known amounts of DBD and DBF in a stirred slurry of unbleached commercial softwood kraft (kappa no. 27.9) in a large volume of water. The ratio of water to methanol was high. The pulp stood for a couple of hours. We filtered it and washed it with water. The pulp spike level was 0.2 ppb DBD and 10 ppb DBF provided all the DBD and DBF remained with the pulp. We performed the chlorination for 30 min at 45°C on the equivalent of 110 g o.d. pulp at 3% consistency with 5.6% chlorine and a kappa factor of 0.2. The final pH was 2.2, and no chlorine remained.

**Oxygen treatment of chlorinated DBD and DBF spiked pulp**

We performed an oxygen bleach of 220 g of the chlorinated pulp described above using 12% consistency, 2% sodium hydroxide added at 110°C, 30 min at 110°C, and 100 psi oxygen pressure. We cooled the reactor for 2.5 h before releasing the pressure at 35°C. The final pH was 10.9. We filtered and washed the pulp. In one of the two oxygen experiments performed, the aqueous filtrate was collected and roughly 50% (870 mL) was analyzed for TCDD and TCDF. We spiked the pulp effluent with TCDD-$^{13}C_{12}$ and TCDF-$^{13}C_{12}$ internal standards, transferred to a 1-L separatory funnel, and extracted with three 60-mL portions of $CH_2Cl_2$. We dried the resulting extract over anhydrous sodium sulfate and concentrated it to approximately 5 mL. We processed the effluent extract through acid and base washing, an acid and base silica column cleanup, an alumina column cleanup, and a carbon column cleanup in a manner identical to previous pulp sample extracts.[1] We analyzed the pulp for TCDD and TCDF similar to the other pulp samples.

**Ozone treatment of chlorinated pulps**

We conducted the ozone treatment of 30 g (o.d. basis) of acetic acid washed (to pH 3) DBD and DBF spiked chlorinated pulp at a 1% level (1.04% applied, 1.01% consumed) for 3.5 min using the conditions described for ozonation of the unchlorinated pulp. The final pH was 3.5.

**Hydrogen peroxide treatment of chlorinated pulps**

We mixed the DBD and DBF spiked chlorinated pulp and chemicals for 1 min and then sealed this in a plastic bag and heated at 60°C for 90 min. The treatment used 12% consistency with 30 g of o.d. basis pulp, 2% hydrogen peroxide, 2% sodium hydroxide, and 0.05% magnesium sulfate. The residuals were 0.09% hydrogen peroxide and 1.18% sodium hydroxide with a pH of 11.5.

**Analysis of pulp samples for chlorinated DBD and DBF**

We prepared triplicate samples of each pulp for analysis. We removed approximately 10 g of pulp from the bulk sample and transferred this to a Soxhlet apparatus thimble along with 60 g of anhydrous sodium sulfate. We spiked the pulp samples with the following internal standards: 2 ng of 2378-TCDD-$^{13}C_{12}$ and 2 ng of 2378-TCDF-$^{13}C_{12}$. We extracted the pulp samples for approximately 18 h with benzene in Soxhlet apparatus. We concentrated the resulting pulp extracts to approximately 5–10 mL. After the addition of 0.8 ng of 2378-TCDD-$^{37}Cl_4$ cleanup standard, the samples underwent acid and base washing, acid and base silica, alumina, and carbon column cleanup. We immediately added a recovery standard, 4 ng of 2378-TCDD-$^{13}C_{12}$, before analysis. We analyzed the samples by high resolution gas chromatography and mass spectroscopy for 2378-TCDD and 2378–TCDF, total TCDD and TCDF, and DBD and DBF as well as chlorine containing compounds having up to 4 chlorine molecules using previously described procedures.[3]

sidual pH and peroxide. We also washed it with water. The oxygen experiment contains large amounts of 2% sodium hydroxide. It is equivalent to an extraction of the pulp. This means that an E–stage type pulp results. In the repeat experiment, we also analyzed the effluent from the oxygen treatment and found 3600 parts per thousand of TCDF and 22 parts per thousand of TCDD. The hydrogen peroxide treatment may also have had TCDF and TCDD in its effluent, but there was no analysis.

The data from this experimental set suggests that post-treatments of pulps containing TCDD and TCDF can lower the PCDD and PCDF pulp contents by 50% and 100%, respectively. Some of the TCDD and TCDF transfers to the effluents, however, suggesting that a posttreatment may not be very effective in destroying PCDD and PCDF.

## Summary

Nitrogen dioxide pretreatment of DBD and DBF spiked cotton linters effectively reduced PCDD and PCDF levels observed after chlorination of the linters. In contrast, ozone appeared ineffective. The ozone treatment used completely dry linters and was probably ineffective because solvent (water) may be necessary for efficient transportation of ozone to reactive sites.

A DBD and DBF spiked pulp gave extremely low levels of TCDD and TCDF using pretreatment with ozone before chlorination. A nitrogen dioxide pretreatment followed by chlorination gave a modest TCDD and TCDF reduction. The result suggests that an ozone bleaching stage before a chlorine or chlorine dioxide bleaching stage may successfully reduce PCDD and PCDF to nondetectable levels.

Posttreatments of dioxin–containing pulps with ozone, hydrogen peroxide, and oxygen led to reductions of about 50% in TCDD and TCDF. The TCDD and TCDF reduction in the pulp was highest for the oxygen treatment; TCDD and TCDF were in the effluent, however. It, therefore, is uncertain whether the treatment destroyed TCDD and TCDF or just redistributed the TCDD and TCDF components.

These research results should provide guidance to the paper industry as changes occur in bleaching technologies to address governmental regulations surrounding the dioxin issue. TJ

The Chlorine Institute provided financial support for this work. We appreciate the assistance of Amy Malcolm, Kyle Reed, and Alexander Shakhet at the Institute of Paper Science and Technology for performing the pulp bleaching reactions involving chlorine, oxygen, nitrogen dioxide, and hydrogen peroxide.

Received for review March 22, 1993.

Accepted Sept. 19, 1993.