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EMISSIONS OF HYDROCHLORIC ACID, CHLORODIOXINS AND CHLOROFURANS FROM THE COMBUSTION OF CHLORINE-CONTAINING KRAFT PULP MILL BLEACH PLANT WASTE

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ABSTRACT

Thermal destruction of waste from a pulp mill bleach plant is a potential alternative to treatment and discharge; however, combustion of chloride and chlorinated organic compounds could result in undesirable air emissions. The objective of this work was to determine if combustion of chlorine-containing bleach plant waste causes emissions of hydrochloric acid, polychlorinated dibenzo-*p*-dioxins, (PCDD) and polychlorinated dibenzofurans (PCDF).

Small additions of chlorine-containing bleach plant waste to normal black liquor feed stock did not result in detectable increases in HCl emissions with incineration. Large additions (≥ 10% by weight of solids) increased HCl emissions, possibly as a direct result of organochlorine combustion. The total PCDD/F in flue gas increased by a factor of ten with a 1% addition of bleach plant concentrate to black liquor. Comparisons of emitted PCDD/F and feed liquor PCDD/F indicated a net formation of PCDD/F during combustion. The emissions of PCDD/F may be a significant factor detracting from the feasibility of thermal destruction of mixtures of chlorine-containing bleach plant waste and black liquor in a standard recovery furnace.

INTRODUCTION

The production of unbleached kraft pulp includes a recovery cycle in which used or "black" liquor from the pulp mill is incinerated and heat and pulping chemicals are recovered. While pulp mill byproducts are easily recovered, waste from bleach plants using chlorine-based bleaching chemicals generally cannot go through the recovery cycle. There is a general concern that incineration of the chlorine-containing effluents will cause harmful air emissions, affect black liquor heating values and rates, and will cause scaling and corrosion in evaporators, heaters, and boilers. Therefore, in the past it

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has been permissible and economical to biologically treat and then discharge bleach plant waste into receiving waters.

However, public and legislative pressure has been growing to discharge cleaner effluents, to reduce water usage, and to reduce the volume of effluent discharged. This trend has renewed the interest of the industry in a "closed mill technology," that is, technology that dramatically reduces or eliminates effluents. One aspect of closed mill technology is the separation of water from solids, using techniques such as ultrafiltration, to allow recycling of clean water. Purification of bleach plant effluents generates a second stream which must be disposed of: the bleach plant solids. The feasibility of thermal destruction of these concentrated streams is a topic of great interest to the pulp and paper industry.

Past research indicates that ultrafiltration concentrates of the first alkaline extraction (E1) stage may be suitable for incineration in a mixture with black liquor (1,2,3). The E1 waste represents 25-50% of the total volume of waste from the bleach plant. The extraction stage solids are composed of approximately 45% carbon, 5% organochlorine, 10% chloride, and 10% sodium, by weight. There is more organochlorine, more chloride, less sodium, and less potassium in these bleach plant solids (BPS) than in black liquor solids. The combustion heating values are comparable to black liquor (1).

Emissions of chlorinated compounds can be significant with the combustion of fuels that contain chlorine. Hydrochloric acid is a common byproduct of combustion of coal, black liquor, and other fuels (4). Emissions of HCl from kraft recovery furnaces range from nondetectable levels to nearly 100 ppm at 8% O_2 (5). Polychlorinated dibenzo-*p*-dioxins and dibenzofurans have also been detected in emissions from municipal waste incinerators (6) and sludge incinerators (7). Reported average emissions of total PCDD and total PCDF from three kraft recovery furnaces were low: 1.2 ng/Nm^3 at 8% O_2 for dioxins and 0.8 ng/Nm3 at 8% O_2 for furans (8). As the chlorine content of the feed increases, the potential for emission of chlorine-containing compounds increases.

The objective of this work was to determine if addition of chlorine-containing bleach plant solids to black liquor solids causes changes in emissions of hydrochloric acid and PCDD/F upon combustion. Experiments were conducted in a laboratory-scale furnace and a small pilot-scale furnace.

EXPERIMENTAL

Effluents

Samples of E1 effluent from the first extraction stage and concentrated black liquor (68% solids) were obtained from a softwood bleached kraft mill using 15-20% ClO_2 substitution. Chlorine-containing concentrate was produced by ultrafiltration of the E1 effluent. Details of the ultrafiltration are given in reference (9). Further concentration of the E1 concentrate to about 65% solids was accomplished in a rotary evaporator under N_2 at 70-85°C. Liquor mixtures were made by combining E1 concentrates with black liquor. The amount of concentrate added is reported as a percentage of total dry solids. Elemental compositions and heating values of the two materials are given in Table 1.

Table 1. Compositions of black liquor and E1 concentrate, wt/wt% of solids.

	Black Liquor	E1 Concentrate
C	36.9	39.2
H	4.71	3.29
O	32.5	32.4
S	4.90	0.51
Na	18.5	14.2
Cl (Org)	–	5.95
Cl (Inorg)	0.46	4.43
HHV	6,320	5,720 (BTU/lb)
NHV	5,250	5,340

Lab Scale Furnace

Emissions of HCl and PCDD/F from the combustion of liquor mixtures were measured using the tube furnace shown in Figure 1. The furnace temperature used for the tests was 800°C. Dry liquor solids (100-200 mg) were placed in a ceramic boat which was inserted through the furnace door into the end of the combustion tube. Air was drawn at 5 slpm through the tube. Average residence time of the gases in the combustion tube was approximately one second, which was considered to be sufficient time for complete combustion of the volatilized gases to CO_2 and H_2O. After combustion of the boat contents (2-5 minutes), the boat was removed and the unburned ash residue was cooled, weighed, and analyzed for chloride.

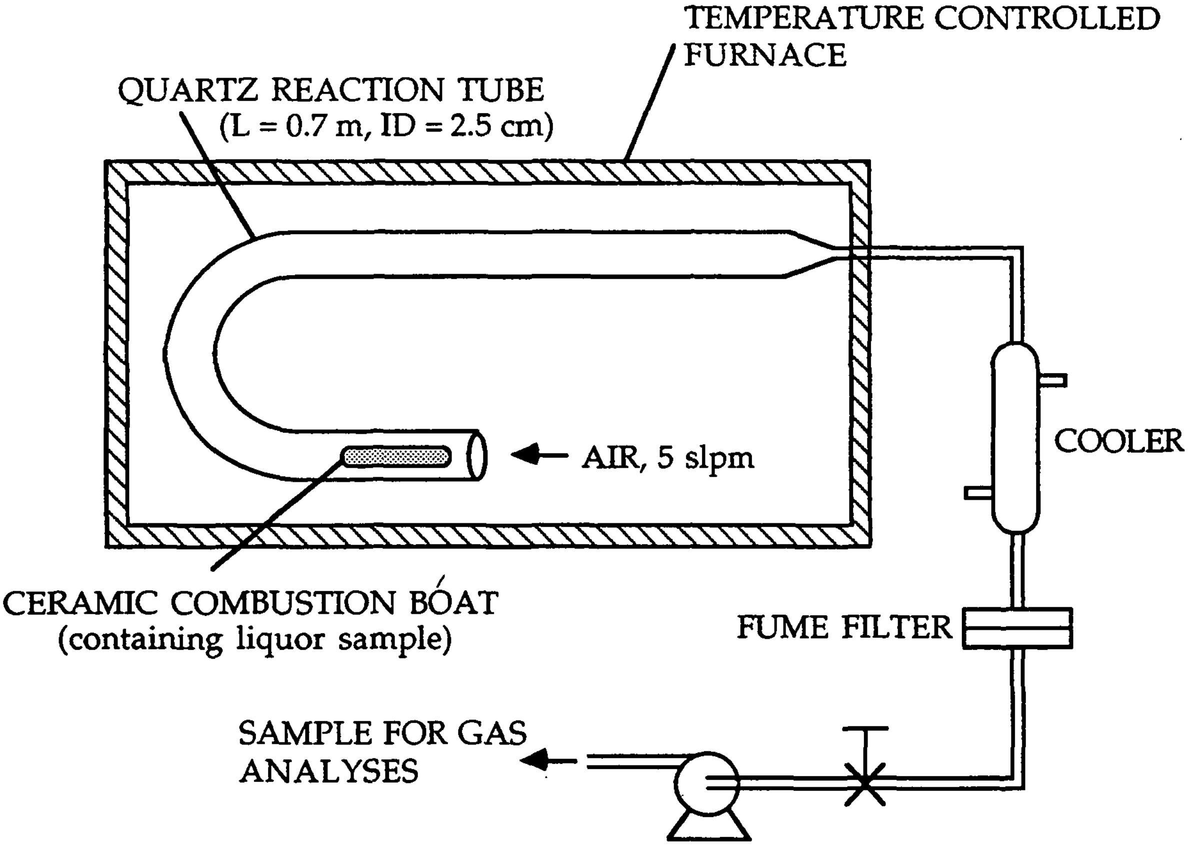

Figure 1. Lab scale combustion furnace.

Mini-Pilot Scale Furnace

Measurements of emissions of PCDD/F during combustion of mixtures of liquor solids were also made using the mini-pilot scale combustion furnace shown in Figure 2. This reactor, which is described in greater detail elsewhere (10), consisted of a vertical tube furnace placed above a char bed furnace. Liquor of approximately 65% solids was converted to droplets by a vibrating feed mechanism on top of the tube furnace. The droplets (2-2.5 mm diameter) fell downward through upward flowing air and

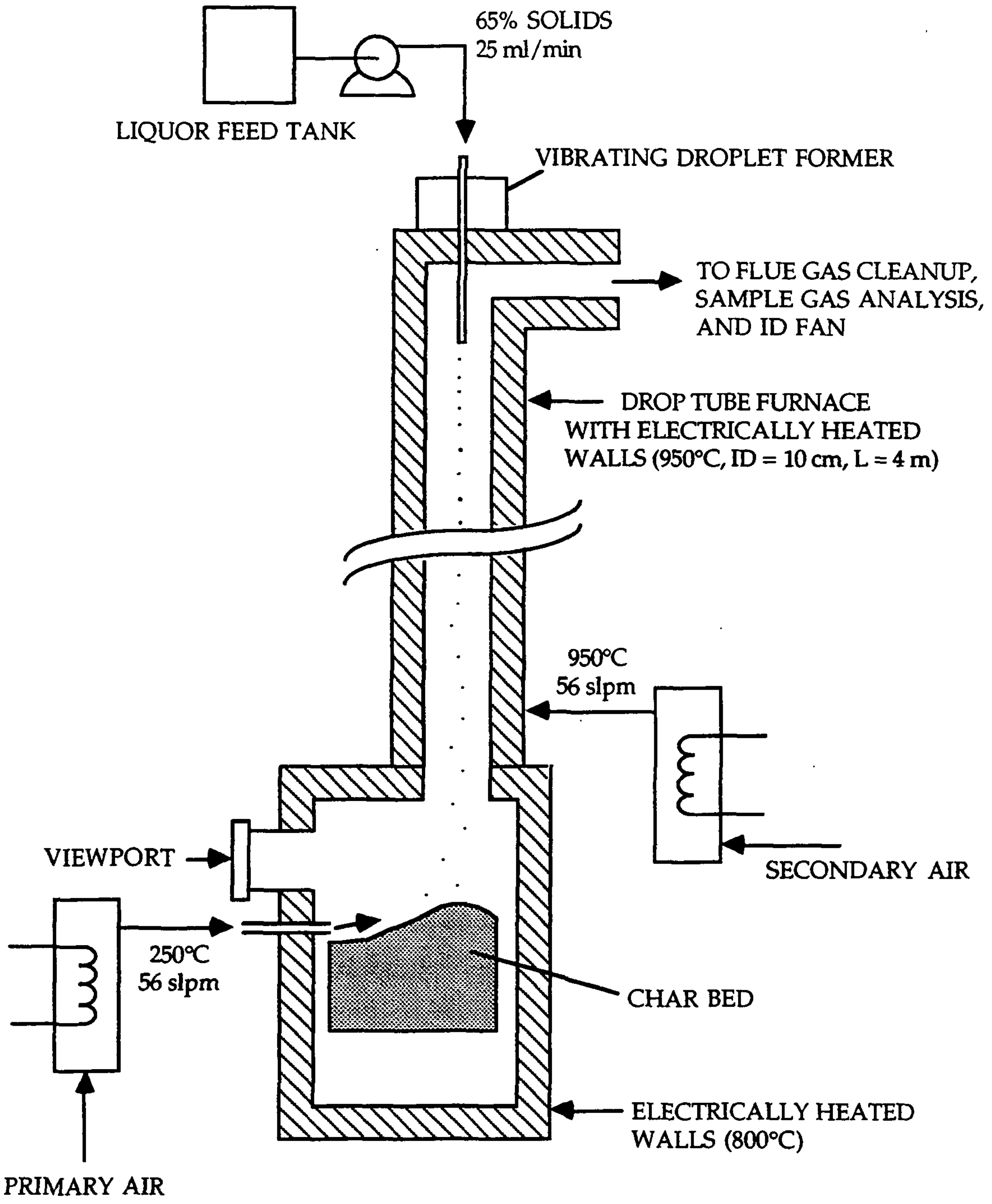

Figure 2. Mini-pilot scale combustion furnace.

combustion product gases. The droplets were heated by convection from the gases and radiation from the furnace walls. Furnace wall temperatures and air preheat temperatures are indicated in Figure 2, and were regulated by electronically controlled electric heaters.

Drying, swelling, partial pyrolysis, and limited char burning occurred as the droplets descended through the tube furnace. The swollen char particles collected in the char bed furnace, where preheated air was directed across the bed surface to complete the combustion. The air split was 50% primary and 50% secondary. The total air rate was set according to the liquor rate, so that there was approximately 20% excess air beyond that required for stoichiometric combustion.

HCl Measurement

Concentrations of HCl in the flue gas were measured for the lab scale combustion tests. The gaseous products of combustion were drawn out of the furnace, filtered, and bubbled through an acidic solution to capture HCl as dissolved chloride (adapted from EPA Method 26 (11)). The chloride concentration of the solution was determined by ion chromatography, using TAPPI Method T699.

The entire flue gas volume (5 slpm) was drawn through the HCl sampling system. Measurements were also made of chloride in the rinsate of the combustion tube, on the fume filter, and in the ash residue remaining in the boat after combustion.

Concentrations of HCl are reported in ppm @ 8% O_2 in dry flue gas. These values can be converted to g/kg (grams of HCl emitted per kilogram of moisture-free solids combusted) by employing a conversion factor of 1 g/kg = 110 ppm @ 8% O_2 in dry flue gas. This conversion factor was determined based on the air requirement for stoichiometric combustion being 4.6 gram of air per gram of liquor solids.

PCDD/F Measurement

The flue gas was drawn out of the furnace and through an impinger filled with glass wool for removal of aerosol and particulates. The impinger was submerged in a constant-temperature ice bath, which served to cool the flue gas to approximately 50°C. The gas outflow from the impinger was drawn through a 15 mm X 30 cm chromatography column packed with 20-25 g prepurified XAD-2 resin (Supelco). All fittings and components of the sampling system to which the flue gas was exposed were made of either quartz or Teflon.

After a combustion test, the XAD-2 columns and impinger contents were extracted and cleaned up using the methods described in EPA RCRA Method 8290 (12). Other sample system components (tubing, etc.) were rinsed with toluene and analyzed. The PCDD/F in the impinger extracts and rinsates contained condensed phase PCDD/F while the XAD-2 extracts contained gas phase PCDD/F. The laboratory scale sampling included rinsates from the combustion chamber which differed from the mini-pilot sampling in which the contents of the combustion chamber could not be analyzed.

Amounts of tetra- through octachlorinated congeners in the sample extracts and toluene rinsates were determined by high resolution gas chromatography/mass spectrometry using selected ion monitoring. Ion ratios and retention times were used for identification. Most of the XAD-2 columns were prespiked with ^{13}C-labeled PCDD/F surrogate standards prior to flue gas sampling in order to monitor sampling efficiency, reproducibility, and recovery. The surrogates included 2,3,4,7,8-pentachlorodibenzofuran (PeCDF); 1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin (HxCDD); 1,2,3,4,7,8-hexachlorodibenzofuran (HxCDF); and 1,2,3,4,7,8,9-(heptachlorodibenzofuran (HpCDF). All of the surrogate recoveries fell between 86% and 99%, meeting EPA criteria for acceptability (11). Coefficients of variation (100 x standard deviation/mean) ranged from 3% to 21%. Surrogates were also spiked into mixtures of the apparatus rinsates and impinger contents prior to extraction. Variability in surrogate quantities in these samples represent analytical variability. Recoveries were between 88% and 105% and coefficients of variation ranged from 6% to 9%. All PCDD/F emission values reported are corrected for analytical recoveries.

Concentrations of PCDD/F are reported in ng/dscm (nanograms of PCDD/F per dry, standard cubic meter, 298 K, 1 atm) normalized to 8% O_2 in the flue gas. These can be converted to pg/g (picograms of PCDD/F emitted per gram of moisture-free solids combusted) by employing a conversion factor of 1 ng/dscm @ 8% O_2 in flue gas = 6.1 pg/g.

For the lab scale tests, concentrations of PCDD/F and concentrations of HCl were not measured simultaneously; separate combustion tests were performed for each.

Toxicity equivalency factors (TEF) based on relative carcinogenicity of the different congeners were used to generate comparisons of toxic equivalences. The values used for TEF are based on Barnes, et al. (13).

RESULTS AND DISCUSSION

HCl Emissions

The combustions in the lab scale furnace indicate the effect of large additions of BPS to black liquor solids on HCl emissions (Figure 3). When 100% BPS was combusted, nearly 600 ppm of HCl was emitted. Despite the high HCl concentrations, this emission represents only 5% of the total liquor chlorine. This result is consistent with earlier reported chlorine trapping data, which showed that most organic chlorine is trapped as NaCl rather than

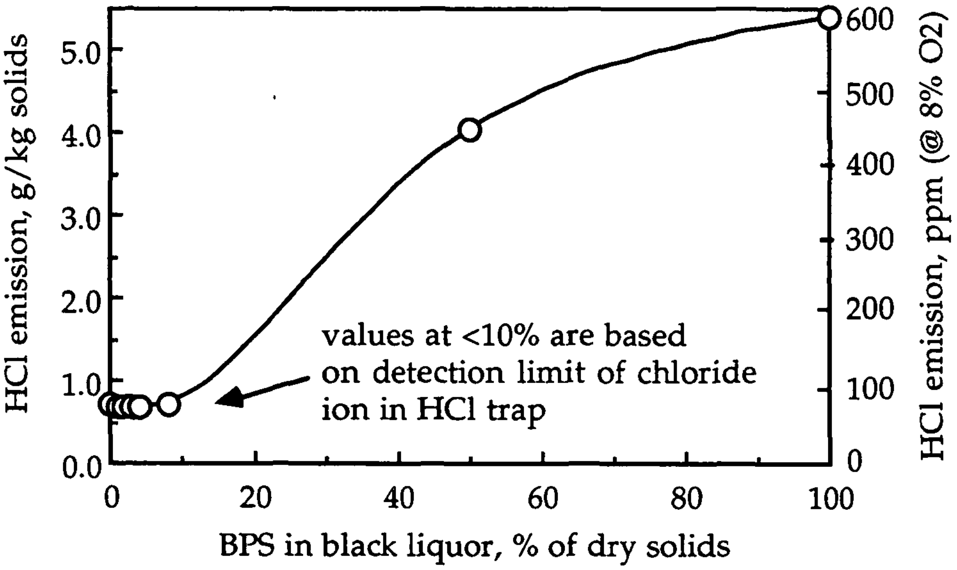

Figure 3. Effect of E1 concentrate addition on HCl emissions from lab scale black liquor combustion.

emitted as HCl during pyrolysis of bleach plant solids that contain a molar excess of sodium over chlorine (1). Levels of BPS less than 10% resulted in HCl emissions less than 80 ppm in the laboratory studies. No detectable increases were noted between 0% and 10% BPS, although sensitivity was limited due to chromatographic interferences. Based on these detection limits, less than 15% of the total chlorine in the black liquor solids (0% BPS) and less than 5% of the chlorine in the 10% BPS mixture was converted to HCl. On average, 55% of the black liquor chlorine was found as chloride in the residue remaining in the ceramic boat after the test, and 33% was found on the filter and the walls of the glass tubing.

Although this work and other research (2) shows that HCl emissions may be limited when there are high molar ratios of sodium to chlorine, it is important to consider the role of sulfur. A major route for the formation of HCl during black liquor combustion occurs when sodium chloride volatilizes from the bed, recondenses in the cooler portions of the furnace, and then reacts with sulfur dioxide, as shown in the following reaction (16).

$$2\,NaCl\,(s) + SO_2\,(g) + 1/2\,O_2\,(g) + H_2O\,(g) \text{ -----> } 2\,HCl\,(g) + Na_2SO_4\,(s)$$

The relatively high S/Na molar ratio in the black liquor (0.18) allows this reaction to occur during normal black liquor combustion. The amount of HCl produced by the sulfur dioxide pathway is highly temperature dependent; lower bed temperatures result in a higher sulfidity in the flue gas (15) which in turn will affect the extent to which NaCl can be converted to HCl.

Because of the relatively low molar ratios of S/Na in the bleach plant solids (0.02) compared to black liquor, formation of HCl by this mechanism is likely to be minimal for mixtures with high levels of bleach plant solids, such as existed in some of the laboratory scale experiments. The increase in HCl production with large increases in BPS levels in the laboratory scale experiments may have resulted from an alternative mechanism, such as direct formation from the combustion of chlorinated organics.

Although the concentrations of the HCl emissions and the average percentage of black liquor chlorine emitted as HCl reported here are consistent with those reported for 12 kraft recovery furnaces (0 - 96 ppm at 8% O_2, 4.7%) (5), the precise level of HCl emissions measured in these tests should not be considered to necessarily represent the HCl emission level of a recovery furnace burning these liquors. Because the time, temperature, and mixing histories of gases and particles in these furnaces will not be the same as those in a given recovery furnace, the emission levels will not necessarily be the same. However, it appears that HCl emissions do not significantly increase with small additions of bleach plant solids.

PCDD/F Emissions

The emissions of gas phase and condensed phase PCDD/F from lab scale and mini-pilot scale combustions are tabulated in Tables 2 and 3.

The combustion of mixtures of bleach plant solids and black liquor solids caused more PCDD and PCDF to be emitted than combustion of black liquor alone. As shown in Figure 4, the addition of 1% BPS to the black liquor increased the amount of total PCDD/F by an order of magnitude for both the lab scale and the mini-pilot tests.

The extent of the effect of 0.5% BPS on PCDD/F emissions is less clear because of differences in mini-pilot scale data and the lab scale data. The mini-pilot scale data for the 0.5% mixture had an unusual pattern of emission for the tetrachlorodibenzofurans compared to the other samples and compared to other typical combustion emissions (17,18) and therefore the data should be viewed with caution. Recoveries of labeled standards and surrogates for the 0.5% BPS mini-pilot scale tests were comparable to the other tests, which suggests that neither sampling nor analytical problems were responsible for the anomaly.

Toxicity equivalences are shown in Figure 5. The result is similar; total toxicity increased by approximately one order of magnitude with the addition of 1% BPS to the black liquor. The toxicity equivalents emitted in the mini-pilot tests were largely due to emissions of 2,3,7,8-TCDF. The most toxic congener, 2,3,7,8 TCDD, was not detected in any of the samples. The increase in emissions of toxicity equivalents reflected higher 2,3,7,8-TCDF emissions as well as emissions of other 2,3,7,8 substituted congeners, particularly PeCDD and PeCDF.

Table 2. **PCDD/F emissions from lab scale combustion of mixtures of BPS with black liquor.**

	0% Bleach Plant Solids			0.5% Bleach Plant Solids			1.0% Bleach Plant Solids		
ng/dscm @ 8% O2	gas	condensed	total	gas	condensed	total	gas	condensed	total
DIOXINS									
2378 TCDD	<0.05	<0.03	<0.08	<0.07	<0.05	<0.12	<0.05	<0.07	<0.12
OTHER TETRA D	<0.05	<0.03	<0.08	<0.07	<0.05	<0.12	<0.05	<0.07	<0.12
PENTA D	<0.05	<0.05	<0.10	<0.10	<0.07	<0.16	<0.03	<0.05	<0.08
HEXA D	<0.08	<0.08	<0.16	<0.10	<0.13	<0.23	<0.05	<0.18	<0.23
HEPTA D	<0.05	7.27 (2)	7.27	<0.10	35.3 (2)	35.3	<0.07	40.4	40.4
OCTA D	<0.03	28.4	28.4	1.36*	176	177	1.33	242	243
TOTAL D	<0.29	35.7	35.7	1.36*	212	213	1.33	283	284
FURANS									
2378 TCDF	<0..03	<0.03	<0.07	<0.05	<0.03	<0.08	<0.05	<0.05	<0.10
OTHER TETRA F	<0.03	<0.03	<0.07	<0.05	0.29	0.29	<0.05	<0.05	<0.10
PENTA F	<0.05	<0.02	<0.07	<0.03	<0.03	<0..07	<0.05	<0.03	<0.08
HEXA F	<0.03	0.47	0.47	<0.03	2.41	2.41	<0.03	2.26	2.26
HEPTA F	<0.02	1.74	1.74	<0.03	11.9	11.9	<0.05	14.9 (2)	14.9
OCTA F	<0.05	2.37	2.37	<0.10	14.0	14.0	<0.07	16.2	16.2
TOTAL F	<0.21	4.58	4.58	<0.29	28.5	28.5	<0.29	33.3	33.3

* Includes a value for EMPC (estimated maximum possible concentration).

Numbers in parentheses represent numbers of congeners if more than one was detected.

Table 3. PCDD/F emissions from mini-pilot scale combustion of mixtures of BPS with black liquor.

	0% Bleach Plant Solids			0.5% Bleach Plant Solids			1.0% Bleach Plant Solids		
ng/dscm @ 8% O2	gas	condensed	total	gas	condensed	total	gas	condensed	total
DIOXINS									
2378 TCDD	<0.01	<0.02	<0.02	<0.01	<0.01	<0.02	<0.01	<0.01	<0.02
OTHER TETRA D	<0.01	<0.02	<0.02	1.47 (2)	0.12	1.59	1.47 (2)	0.29	1.76
PENTA D	<0.03	<0.01	<0.04	<0.01	<0.01	<0.02	1.08 (2)	0.27	1.34
HEXA D	<0.01	<0.01	<0.02	<0.01	<0.01	<0.02	<0.02	<0.01	<0.02
HEPTA D	<0.02	<0.02	<0.04	<0.04	0.09	0.09	<0.02	0.28	0.28
OCTA D	<0.02	0.21	0.21	0.05	0.59	0.64	<0.02	0.54	0.54
TOTAL D	<0.11	0.21	0.21	1.52	0.80	2.32	2.54	1.38	3.92
FURANS									
2378 TCDF	0.54	0.09	0.62	0.34	<0.01	0.34	1.96	0.68	2.64
OTHER TETRA F	-	-	-	0.24	<0.01	0.24	8.31 (10)	1.61 (7)	9.92
PENTA F	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	5.38 (6)	2.84 (8)	8.21
HEXA F	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	1.08 (4)	2.15 (4)*	3.23*
HEPTA F	0.11*	<0.01	0.11*	<0.01	<0.01	<0.02	0.48	0.54	1.02
OCTA F	<0.04	<0.01	<0.05	<0.02	<0.01	<0.03	<0.01	0.09	0.09
TOTAL F	0.64*	0.09	0.73*	0.59	<0.03	0.59	17.20	7.92*	25.11*

* Includes a value for EMPC (estimated maximum possible concentration).

Numbers in parentheses represent numbers of congeners if more than one was detected.

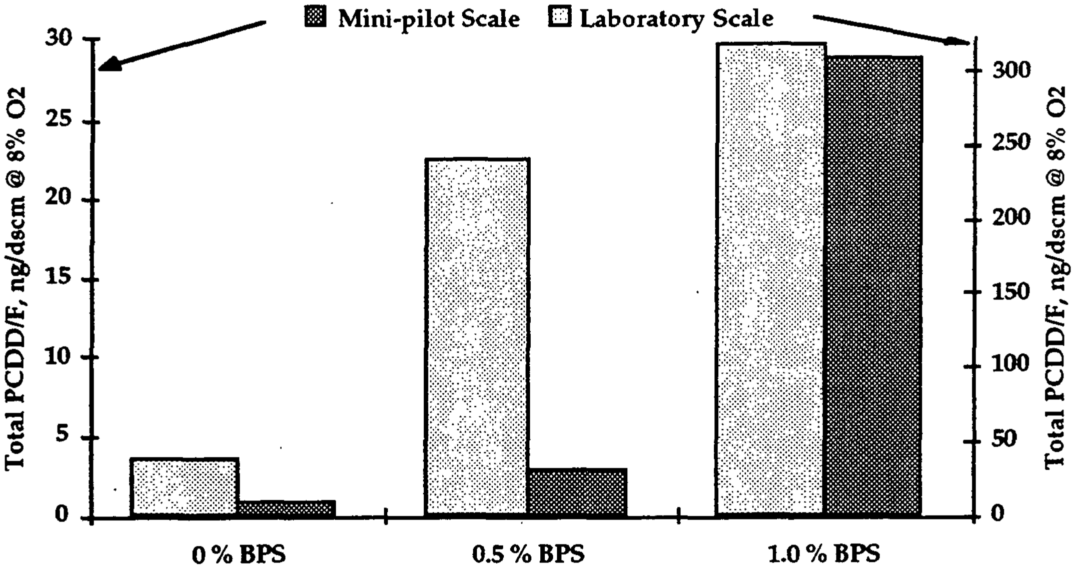

Figure 4. Effect of E1 concentrate addition on total PCDD/F emissions from mini-pilot scale and lab scale black liquor combustion.

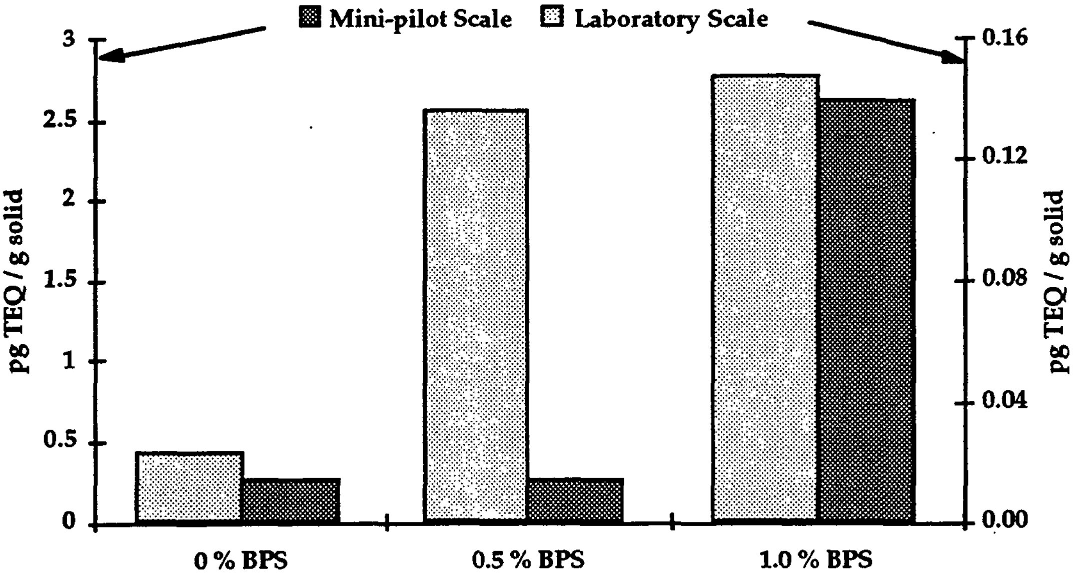

Figure 5. Effect of E1 concentrate addition on PCDD/F toxicity equivalents from mini-pilot scale and lab scale black liquor combustion.

Potential sources of PCDD/F in flue gas include 1) survival of feed stream PCDD/F, 2) coupling of chlorinated aromatics, including chlorophenols, during combustion and, 3) de novo synthesis in which nonchlorinated compounds dissimilar in structure to PCDD/F react and become chlorinated to form PCDD/F (19-21). All of these mechanisms are possible in the combustion of the complex mixtures investigated in this study.

In most cases, concentrations of PCDD/F in both the uncombusted black liquor and the E1 concentrate were not at levels high enough to account for the PCDD/F emitted during combustion. The concentration of total PCDD/F in the black liquor was 56 x 10^{-15} mole/g solids and the concentration in the bleach plant concentrate was 835 x 10^{-15} mole/g solids. In Table 4, these feed levels are compared to the total PCDD/F measured in the combustion emissions. Total mole PCDD/F per g of solids burned are compared because one class of PCDD/F can serve as a precursor to another (e.g., furans can be converted to dioxins, TCDD can be converted to OCDD).

Table 4. Comparison of total PCDD/F in the liquor mixtures to that emitted from lab scale and mini-pilot scale combustion (all values in 10^{-15} mole/g solids).

	0% BPS	0.5% BPS	1.0% BPS
Feed liquor	56	60	64
Emissions, mini-pilot scale	12	44	413
Emissions, lab scale	548	3277	4291

At 1% BPS, levels of emitted PCDD/F exceeded the levels of feed PCDD/F by one order of magnitude for the mini-pilot scale tests, and by two orders of magnitude for the lab scale tests. In the lab scale experiments, the amounts of emitted PCDD/F were 10 times greater than the feed levels for the black liquor and 50 times greater for the 0.5% mixture. It is clear that PCDD/F formation occurred in these instances.

By contrast, emitted PCDD/F levels were less than feed levels during the combustion of black liquor and the 0.5% BPS mixture in the mini-pilot studies. This result may reflect either a net destruction of PCDD/F during mini-pilot scale combustion of the black liquor and the 0.5% mixture or a lack of recovery of particulate-associated PCDD/F. Because large increases in emitted levels were observed with increased BPS even when the feed concentrations of total PCDD/F were similar, it seems unlikely that the increase was simply due to feed PCDD/F. Therefore, it is probable that there was incomplete recovery of particulate-associated PCDD/F in the mini-pilot experiments.

The congener distributions are shown for PCDD (Figure 6) and PCDF (Figure 7) in the emissions from the mini-pilot scale combustion. For comparison, the distributions of PCDD and PCDF in the 1% BPS feed are included (recall from Table 3 that feed concentrations are nearly the same for 0%, 0.5%, and 1.0% BPS). The congeners OCDD, OCDF, and HpCDF dominated the composition of the feed. The major congeners in the emissions were not as highly chlorinated. The concurrent decrease in OCDD levels and increase in the less chlorinated congeners with higher BPS suggests that dechlorination of the OCDD may have been the source of some of the

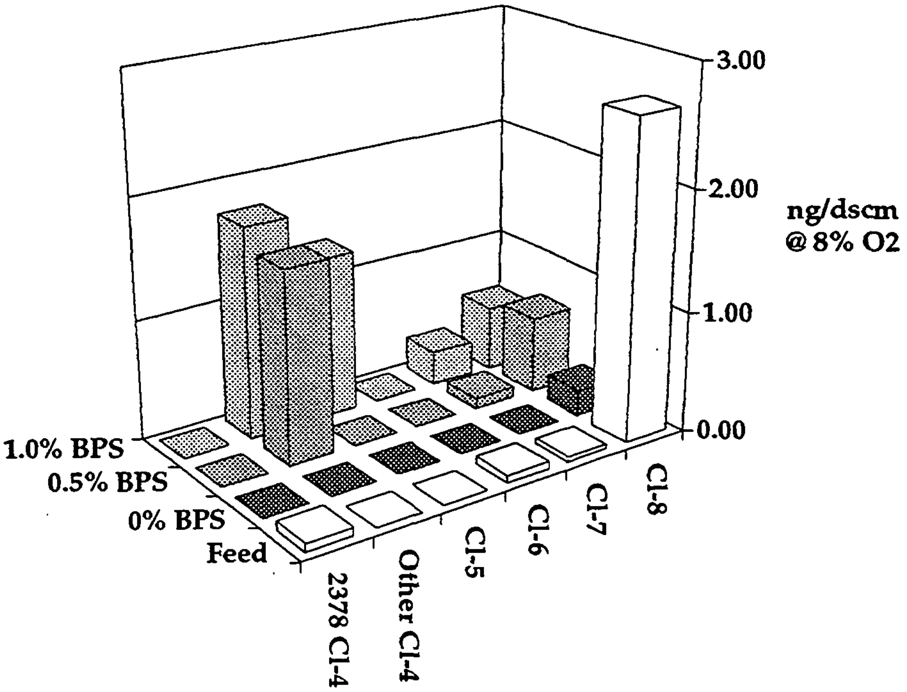

Figure 6. PCDD emissions from mini-pilot scale combustion of liquor mixtures (also included for comparison are feed PCDD levels).

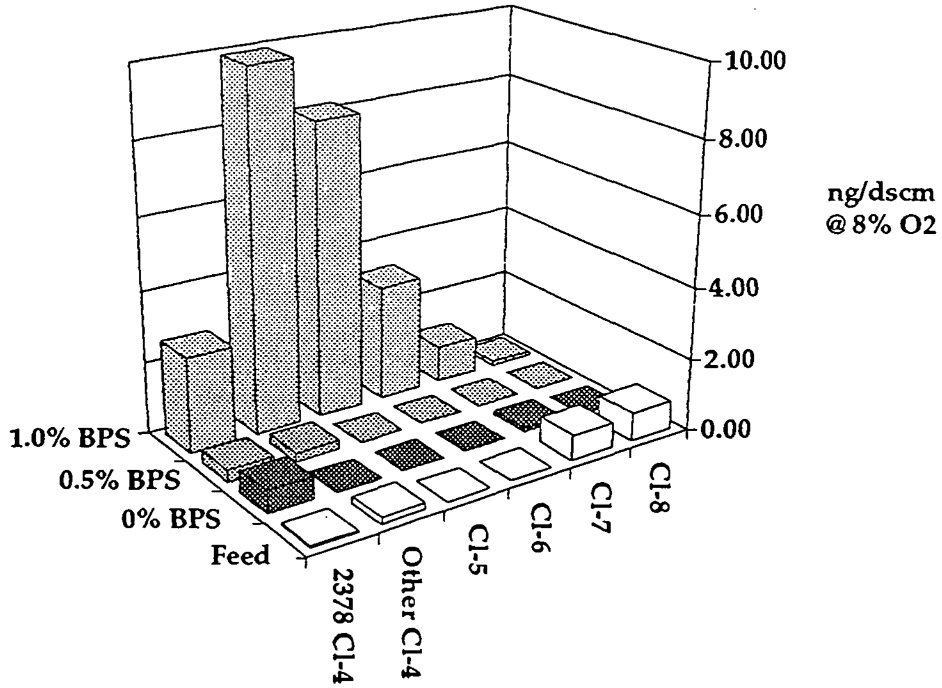

Figure 7. PCDF emissions from mini-pilot scale combustion of liquor mixtures (also included for comparison are feed PCDF levels).

less chlorinated congeners. However, the less chlorinated congeners only became prevalent in the emissions from the combustion of 0.5% and 1.0% BPS mixtures; they were not prevalent in the emissions from the combustion of black liquor alone. Therefore, constituents of the BPS may have promoted dechlorination of OCDD. Alternatively, recovery of particulate-associated OCDD in the feed may have been poor. In the case of the furans, there was not enough OCDF in the feed to account for the less chlorinated congeners.

The distribution of PCDD and PCDF congeners found in the lab scale tests is shown in Figures 8 and 9. The overwhelming predominance of the hepta- and octachlorinated congeners in the lab scale emissions, in contrast to the mini-pilot and other combustion emissions (17,18), suggests that reactions occurred that were peculiar to the lab scale combustion system. The feed distribution could not be solely responsible for the distribution because of the considerably higher levels emitted. A possible explanation is that the fused quartz of the reactor promoted formation of Cl_2. This has been shown to occur by way of the following reactions (22).

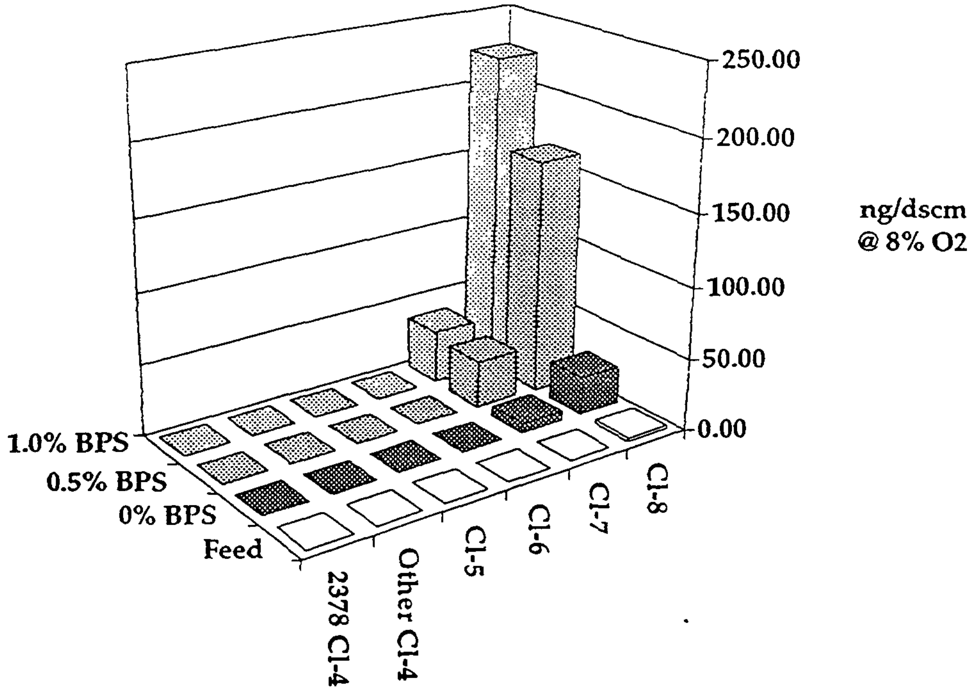

Figure 8. PCDD emissions from lab scale combustion of liquor mixtures (also included for comparison are feed PCDD levels).

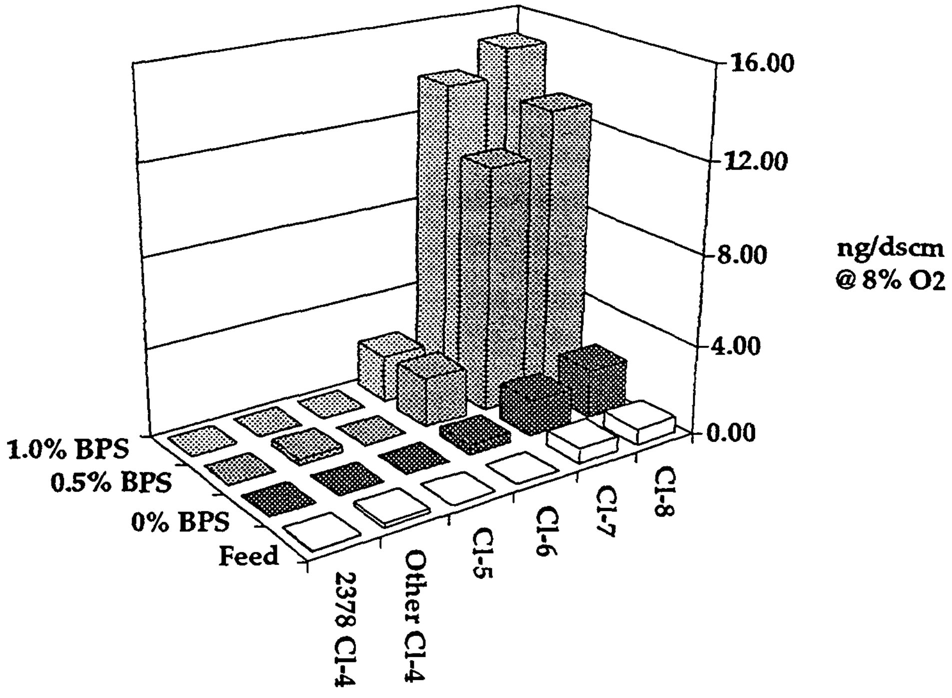

Figure 9. PCDF emissions from lab scale combustion of liquor mixtures (also included for comparison are feed PCDF levels).

$4x\ NaCl + y\ SiO_2 + x\ O_2 \longrightarrow 2x\ Na_2O{,}ySiO_2 + 2x\ Cl_2$

$2x\ NaCl + y\ SiO_2 + x\ H_2O \longrightarrow x\ Na_2O{,}ySiO_2 + 2x\ HCl$

$4\ HCl + O_2 \longrightarrow 2\ H_2O + 2\ Cl_2$

Higher levels of molecular chlorine could have produced more highly chlorinated PCDD/F. It is interesting that HpCDD/F and OCDD/F dominated the PCDD/F distribution in the lab scale tests when so few other chlorinated congeners were detected. This suggests that the availability of the OCDD/F precursors were limited since lower chlorinated congeners were not detected.

Potential precursors to emitted PCDD/F are chlorophenols which were measured in the bleach plant solids. There was approximately 200 nmole chlorophenols per gram of concentrate solids, or 2 nmole chlorophenols per gram of 1% BPS mixture. Although this concentration is high enough to account for the production of the measured PCDD/F on a mass balance basis, it may be too low to allow a fast enough coupling rate to account for PCDD/F formation. It is possible that chlorophenols reacted with other aromatics present in the liquor mixture to produce some of the PCDD/F that were detected in the combustion emissions.

Overall, considerably lower amounts of total PCDD/F emissions were detected from the mini-pilot scale tests than from the lab scale tests. There are at least three possible reasons for the differences between the two systems. The lower temperature of the laboratory tests (800°C compared to 950°C) may have resulted in less destruction of feed PCDD/F. Second, much of the PCDD/F that was originally present and/or newly formed in the mini-pilot furnace may have been associated with particulates which adhered to combustion walls or otherwise were not emitted from the furnace. As described previously, in the lab scale tests the entire combustion chamber was cooled and toluene-rinsed after each individual test, while it was impractical to toluene-rinse the mini-pilot scale combustion chamber. A third possibility is that higher quantities of chlorine in the lab scale experiments generated from quartz-promoted reactions may have produced more PCDD/F.

SUMMARY

Adding small amounts (10% by weight of solids) of chlorine-containing E1 concentrate to black liquor resulted in a feed with high amounts of inorganic and organically-bound chlorine, but incineration of the mixtures resulted in the release of less than 5% percent of the feed chlorine as HCl. Because the sodium to chloride molar ratio was high, the bulk of the chlorine was trapped as sodium chloride. Incineration of high levels (≥ 10% by weight of solids) in the laboratory scale combustions resulted in an increase in HCl emissions, possibly as a result of organochlorine combustion.

Flue gas emissions of total PCDD/F increased approximately tenfold with a 1% addition of bleach plant concentrate to the black liquor in both the lab scale and the mini-pilot scale black liquor combustion experiments. Amounts of PCDD/F in the feed liquor were much less than amounts in the combustion emissions and congener distributions were substantially different. These results indicate that PCDD/F formed during combustion and emissions were not a result of the survival of feed PCDD/F. Lab scale tests yielded greater total levels of PCDD/F and higher levels of the more chlorinated congeners than the mini-pilot scale tests. The differences may have been due to differences in combustion temperatures, differences in sample collection, or interactions with the quartz reactor.

The emissions of PCDD/F may be a significant factor detracting from the feasibility of combining chlorinated bleaching effluents with black liquor for disposal in the recovery furnace; although, it must be noted that values of residence times and temperatures for these combustion tests were less than the times and temperatures in a recovery furnace.

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