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Experimental Study on the Effect of SO₂ on PCDD/F Emissions: Determination of the Importance of Gas-Phase versus Solid-Phase Reactions in PCDD/F Formation

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Cofiring coal in municipal solid waste incinerators (MSWIs) has previously been reported to reduce polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/Fs) emissions due to increasing the flue gas SO₂ concentration. The present study was focused on understanding the primary mechanism responsible for the suppressant effect of SO₂ on total PCDD/F formation and toxic equivalent (TEQ) emissions. The addition of SO₂, simulating the effect of coal addition on the flue gas composition, resulted in significant reductions in the TEQ emissions due to reactions involving SO₂ in the postcombustion zone. However, emissions of total PCDDs/Fs, unlike the TEQ value, were dependent upon the Cl₂ and SO₂ injection temperatures due to increases in non-TEQ correlated isomers. The conversion of metal chlorides in the fly ash to sulfates, thus reducing the sites responsible for chlorination/oxidation reactions, was concluded to be the main suppressant mechanism; proposed reactions for copper and iron are presented. This mechanism was found to be independent of combustion conditions and could have prolonged effects on PCDD/F emissions from deposits formed with high flue gas S/Cl ratios.

Introduction

With the rapid development of its economy, many cities in China are experiencing environmental pollution problems caused by improper disposal of municipal solid waste (MSW). MSW thermal treatment technologies, such as fluidized bed and stoker incinerators, have been considered as primary methods for volume reduction, safe disposal, and energy recovery. However, the complexity of Chinese MSW (variable densities, high moisture, and low heating values) makes it difficult to maintain stable combustion. Cofiring up to 20 wt

% of coal has been reported to result in a significant reduction in PCDD/F emissions from incinerators in China (1, 2), Europe (3, 4), the U.S.A. (5), and in laboratory scale units (6–9). This reduction may be due in part to improved combustion efficiency but has also been linked to the suppressive effect of SO₂.

Several mechanisms have been proposed to explain the effect of SO₂ on PCDD/F formation: (i) homogeneous reduction of Cl₂ to HCl (10) (Cl₂ has been suggested to be important in PCDD/F formation (11)), (ii) poisoning of the catalytic sites involved in the Deacon process (12) which has been shown to convert HCl to Cl₂, (iii) conversion of metal oxide/chloride catalyst sites to metal sulfates that are less active in biaryl synthesis (i.e., PCDD formation from phenol) (12), and (iv) sulfonation of the phenolic PCDD and PCDF precursors to form sulfonated analogues of PCDDs/Fs (13).

With regard to (i), Griffin (10) proposed that the presence of SO₂ enhanced the conversion of Cl₂ to HCl



via a homogeneous mechanism. The postulated importance of R1 in PCDD/F suppression is due to the reported relationship between Cl₂ and PCDD/F formation (11). R1 was concluded to have resulted in a 30% conversion of Cl₂ to measured HCl at temperatures as low as 400 °C (14). Other work has shown R1 to occur measurably only at temperatures of at least 750 °C (12, 15).

Gullett et al. (12) suggested that SO₂ could react with the Deacon process catalyst (CuO) and form copper sulfate (CuSO₄); however, Cl₂ production from HCl was reported with both CuO and CuSO₄ albeit with different temperature dependencies. Raghunathan and Gullett (14) reported that PCDD/F inhibition more likely occurred via R1 since a difference in HCl conversion to Cl₂ over CuO (at 400 °C) was not observed to be affected by the addition of SO₂ either before or after the catalyst bed.

Reduced formation of PCDDs from the reaction of phenol over CuSO₄, compared to CuO, was attributed (12) mainly to a reduced activity of CuSO₄ to catalyze the biaryl condensation reaction rather than via R1 competition with the Deacon process. Addition of SO₂ to the reacting gas (phenol in O₂/N₂) over CuO showed no effect, although water vapor was not added to the gas-stream; thus, R1 was not possible. Additionally, many sulfur-containing organics were formed when fly ash was spiked with elemental sulfur and then heat-treated in moist air at 300–500 °C (16); a decrease in PCDD/F formation was not observed.

While evidence is definitive as to the suppressant effect of increased SO₂ concentrations in combustion flue gas (i.e., due to coal cofiring with MSW) on PCDD/F emissions, the mechanism(s) responsible for this reduction remains elusive. The aim of this investigation is to assess the importance of gas-phase and surface reactions in the presence of flue gas SO₂ leading to reductions in PCDD/F emissions. A MSW incinerator was simulated under normal and upset conditions, with and without the presence of soot, using an entrained (fly ash) flow reactor. The key mechanism(s) by which SO₂ affects PCDD/F emissions were addressed at the combustor (1000 °C) and postcombustor (400 °C) regions to discern the potential for different suppression mechanisms.

Experimental Section

The experiments for this study were conducted in an entrained flow reactor (EFR) designed to simulate the combustion and postcombustion regions of a MSW incin-

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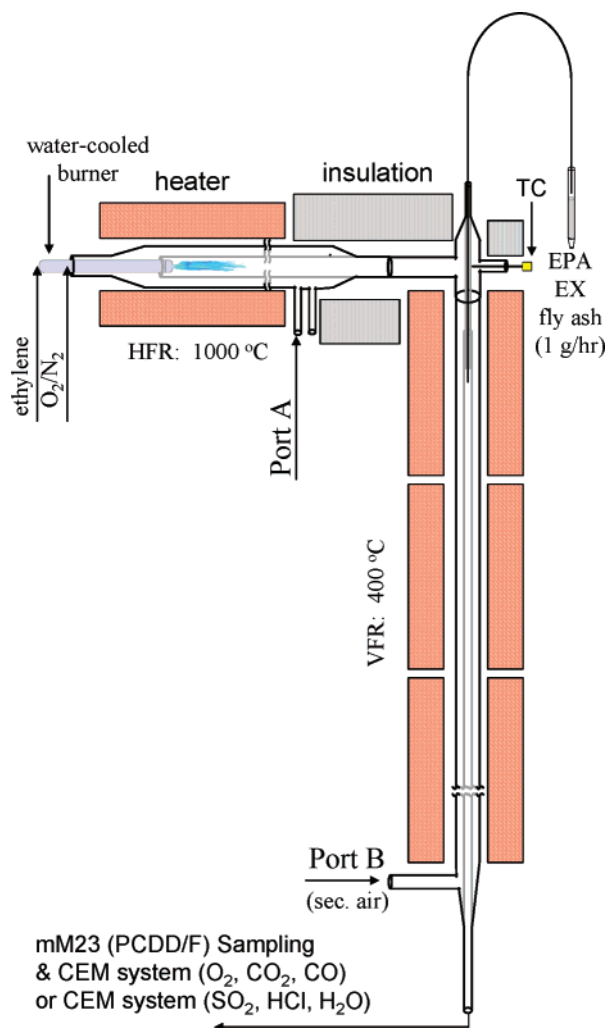


FIGURE 1. Schematic of the entrained flow reactor (EFR), not to scale.

erator (see Figure 1). The details of the reactor system are discussed elsewhere (17). Chlorine (Cl_2/N_2) and sulfur dioxide (SO_2/N_2) can be fed into either the flame zone (port A) or directly into the postcombustion zone (port B); in either case the gas is preheated through the annulus of the quartz reactors before mixing with the bulk gas. For example, port B is located at the bottom of the vertical reactor; the inlet gas flows vertically up through the annulus of the concentric tube for preheating before mixing with the combustion gas and fly ash at the top of the postcombustion zone. Fly ash is fed into the postcombustion zone in 100 mL/min of nitrogen from a mechanically vibrated fly ash hopper (partially fluidized bed).

For this work, a premixed ethylene-air flame was operated in the combustion section using a water-cooled burner. The equivalence ratios (Φ) used were 1.33 (nonsooting) and 1.87 (sooting); the incipient sooting Φ was determined to be 1.79, in agreement with that listed by Glassman (18). The temperatures of the horizontal (combustion zone) and vertical (postcombustion) section of the EFR were maintained at 1000 and 400 °C, respectively. Supplemental air was added through port B to bring the oxygen concentration in the flue gas to 6–8%. The residence times of the gas in the horizontal and vertical sections were 0.9 and 1.3 s, respectively. A toluene-extracted (24 h), hexane-washed, N_2 -dried fly ash, collected from the electrostatic precipitator (ESP) of a grate-fired MSW incinerator, was used in this study. This fly ash, denoted as EX ash, is the same as that used by Wikström et al. (17, 19)

in their EFR studies. The properties of the fly ash have been reported previously (17); in summary, the fly ash contains (by weight) 1.0% C, 5.7% chloride, 0.17% Cu, 0.95% Fe, and 6.4 ppm S.

The test matrix (Table 1) consists of a total of 17 EFR tests; each test was conducted in two 2-h segments ("A" followed by "B"). The B samples were used to investigate the prolonged effects (so-called memory effects) from the run A conditions of fly ash feeding, sooting, and SO_2 addition. Only B samples relevant to that goal are reported here. The parameters changed during testing were SO_2 concentration, flame characteristics (no flame, nonsooting flame, and sooting flame), fly ash feeding, Cl_2 addition, and the ports of entry for both SO_2 and Cl_2 .

The sampling and analysis for mono-octa PCDDs/Fs were performed according to an adapted version of U.S. EPA modified method 23 (mM23) described elsewhere (17). The data analysis included all 210 PCDD/F congeners. The PCDD/F results are presented in units of pmoles PCDD/F $\text{g}_{\text{EX}}^{-1} \text{dscm}^{-1}$; g_{EX} is grams of EX fly ash fed during the experiment. The units of dscm were calculated using a standard temperature and pressure of 20 °C and 1 atm, respectively. The degree of chlorination was calculated on a molar basis to indicate the mono-octa homologue distribution; for example, if all OCDD or OCDF was formed, PCDD and PCDF would each have degrees of chlorination of 8.0.

For all runs except 10 and 11, fly ash was fed during the A run and stopped prior to the start of sampling for the B run. During the feeding, most of the fly ash remained entrained in the carrier gas and was collected in the EFR emissions during sampling; the remainder ($25 \pm 10.4\%$) was unavoidably deposited on the reactor walls. The measured emissions included PCDDs/Fs adsorbed on entrained (or re-entrained) particles and those in the gas phase (e.g., desorbed from the deposits); the emissions did not include the PCDDs/Fs remaining on the deposits after the A or B runs. Thus, with the exception of runs 10 and 11, the measured emissions in the B runs were due to formation from the residual deposits (PCDD/F on re-entrained fly ash or desorbed into the reactor gas). Therefore, the measured emissions in the B runs were also calculated in units of pmoles $\text{g}_{\text{EX}}^{-1} (\text{deposit}) \text{dscm}^{-1}$, where $\text{g}_{\text{EX}} (\text{deposit})$ is the amount of residual fly ash remaining on the reactor walls after the A run. Emissions reported in these units better reflect release from or re-entrainment of fly ash remaining in the system during the B-run. While the gas residence time is 1.3 s in the postcombustion zone, this value does not reflect the residence time of the fly ash in the postcombustion region. The residual fly ash deposits responsible for PCDD/F emissions at the exit of the postcombustion zone have residence times ranging from 0–120 min for the A runs and up to 240 min for the B runs.

The O_2 , CO_2 , and CO concentrations in the flue gas were measured continuously throughout the experiments using conventional continuous emissions monitors (CEMs) to ensure reproducible operation of the EFR; all CEMs were calibrated before and after each experiment. In addition to the Table 1 test matrix, some experiments were performed to investigate the interaction of Cl_2 , SO_2 , and fly ash in the EFR via measurements of SO_2 , HCl, and H_2O at the exit of the postcombustion zone. These constituents were measured using the Bodenseewerk MCS-100 CEM system to determine the conversion of Cl_2 to HCl and the effect of SO_2 and fly ash on this conversion. These measurements were also made prior to and after each segment (A and B) of the experiments described in Table 1 to ensure that the desired/expected concentrations of SO_2 and HCl were obtained and unchanged. It should also be noted that since the vertical reactor had been used for previous fly ash feeding experiments, none of these tests can be claimed to be done in a strictly homo-

TABLE 1. Experimental Conditions and Results

test	sampling duration [min]	Cl ₂		SO ₂		flame conditions ^b	[pmoles/g _{EX} dscm]		[pmoles/g _{EX} (deposit)/dscm]		degree of chlorination		description
		concn [ppm]	port ^a	concn [ppm]	port ^a		PCDD	PCDF	PCDD	PCDF	PCDD	PCDF	
1A-1	120	none	n/a ^f	none	n/a ^f	nonsooting	381	2942	n/r ^g	n/r ^g	4.1	2.8	baseline: nonsooting flame (no Cl ₂)
2A-1	120	109	B	none	n/a ^f	nonsooting	1261	8827	n/r ^g	n/r ^g	4.7	3.7	addition of Cl ₂ postcombustion (no SO ₂)
2B-1	120	109	B	none	n/a ^f	nonsooting	56	278	363	1798	6.1	4.7	prolonged emissions from wall deposits ^e
3A-1	120	109	B	109	B	nonsooting	910	5183	n/r ^g	n/r ^g	4.4	3.6	SO ₂ concn study: ~100 ppm
4A-2	120	109	B	226	B	nonsooting	719	3168	n/r ^g	n/r ^g	4.4	3.4	SO ₂ concn study: ~225 ppm
4B-2	120	109	B	none	n/a ^f	nonsooting	52	101	202	391	4.9	5.2	effect of SO ₂ during A-run on wall deposits
5A-2	120	109	B	55	B	nonsooting	1181	6243	n/r ^g	n/r ^g	4.9	3.9	SO ₂ concn study: ~55 ppm
5B-2	120	109	B	none	n/a ^f	nonsooting	61	151	165	410	5.6	4.6	SO ₂ during A-run: effect on wall deposits
6A-1	120	109	A	none	n/a ^f	nonsooting	855	5611	n/r ^g	n/r ^g	4.2	3.3	addition of Cl ₂ into flame zone (no SO ₂)
6B-1	120	109	A	none	n/a ^f	nonsooting	32	231	126	923	5.2	3.6	prolonged emissions from wall deposits ^e
6A-2	120	109	A	none	n/a ^f	nonsooting	973	5552	n/r ^g	n/r ^g	4.3	3.7	repeat of 6A-1
7A-1	120	109	A	104	A	nonsooting	725	5306	n/r ^g	n/r ^g	3.8	2.8	SO ₂ /Cl ₂ addition into flame zone
8A-1	120	105	B	104	A	nonsooting	863	5100	n/r ^g	n/r ^g	4.5	3.4	Cl ₂ into postcombustion/SO ₂ into flame
9A-1	120	105	A	104	B	nonsooting	870	5912	n/r ^g	n/r ^g	3.6	3.0	Cl ₂ into flame/SO ₂ into postcombustion
10A-1	120	105	B	104	B	nonsooting	1287	7871	n/r ^g	n/r ^g	4.6	3.6	repeat of 3A-1; for below
10B-1	120	105	B	none	n/a ^f	nonsooting	58	210	170	610	5.7	4.3	continued fly ash feeding in B-run
11A-1	120	107	B	104	B	nonsooting	1324	8321	n/r ^g	n/r ^g	4.5	3.5	repeat of 3A-1; for memory effect test
11B-1	120	107	B	none	n/a ^f	nonsooting	1466	9613	5590	36653	5.1	4.0	memory effect test (no test 3B-1)
12A-1	120	107	B	none	n/a ^f	none	1751	3395	n/r ^g	n/r ^g	7.2	6.7	baseline: no flame, absence of water
13A-1	120	107	B	107	B	none	1695	2442	n/r ^g	n/r ^g	7.2	6.6	no flame: absence of water (no R1)
14A-2	120	119	B	none	n/a ^f	sooting	2115	37904	n/r ^g	n/r ^g	4.9	4.4	baseline: sooting flame
15A-1	120	119	B	109	B	sooting	1805	12096 ^c	n/r ^g	n/r ^g	4.7	3.6	SO ₂ addition during sooting
16A-1	120	119	B	109	B	sooting	1590	5513 ^d	n/r ^g	n/r ^g	5.0	4.3	SO ₂ addition during sooting (repeat 15A-1)
20A-1	120	105	B	216	B	none	1239	3101	n/r ^g	n/r ^g	6.8	4.5	no flame: absence of water (no R1)

^a Port A was into the flame zone (1000 °C), and port B was into the postcombustion zone (400 °C). ^b The nonsooting flame was run at $\Phi = 1.33$, and the sooting flame was run at $\Phi = 1.87$. ^c Quantification of all TeCDD, some DiCDF, and some TeCDF isomers was not possible due to interferences. ^d Quantification of all TeCDD, some DiCDF, all TriCDF, and some TeCDF isomers was not possible due to interferences; the difference between 15A-1 and 16A-1 was likely due to "losses" of more DiCDFs and all TriCDFs (see Table 4 for more information). ^e B-runs were for the "memory effect tests" (i.e., prolonged effect of the conditions during the A-run on subsequent PCDD/F emissions during the B-run, from the wall deposits). ^f n/a: not applicable. ^g n/r: not reported in such units.

geneous reaction environment; prior work has shown residual catalytic activity of the quartz reactor due to interaction with metals in the fly ash even after rigorous cleaning (20).

The formation of metal chlorides and sulfates was investigated in a fixed bed reactor tube by treating 4 g of a mixture of 0.2 wt % copper oxide (CuO), 1.1 wt % iron oxide (Fe₂O₃), and bulk silica (SiO₂) at 300 °C in a flow containing Cl₂, SO₂, or Cl₂/SO₂ for 30 min. A carrier flow of 10% O₂/8% H₂O/N₂ was used for these experiments, with Cl₂ or SO₂ added upstream of the bed. Copper, iron, chloride, and sulfur (as SO₃) concentrations (mg/g) were analyzed in the mixture before and after reaction by a wavelength dispersive sequential X-ray fluorescence analyzer (XRF).

Results and Discussion

The baseline test (without added Cl₂ or N₂) of the EX fly ash reactivity showed emissions of PCDD and PCDF in the combustion gas of a nonsooting ethylene flame ($\Phi = 1.33$) of 380 and 2940 pmoles g_{EX}⁻¹ dscm⁻¹, respectively (see Table 1, run 1A-1). The addition of Cl₂ to the combustion gas in the postcombustion zone (port B, 400 °C) resulted in a greater than 3-fold increase in PCDDs/Fs (Table 1, run 2A-1). The degree of chlorination increased from 2.8 to 3.7 and 4.1 to 4.7 for the PCDFs and PCDDs, respectively. The reactions involved may include the direct chlorination of the carbon structures involved in formation (e.g., single-ring aromatic precursors or larger PAHs and oxygenated PAHs) or the formation of metal chlorides, such as copper and iron chlorides, which subsequently react with the carbon structures (e.g., larger PAHs and particulate carbon).

Effect of Postcombustion Zone (Port B) SO₂ Addition on PCDD/F Emissions. To determine the effect of the SO₂ flue gas concentration on the above results, 55–226 ppm SO₂ was added to the isothermal postcombustion zone (400 °C; through port B), allowing for potential reactions with the combustion gas, Cl₂, and fly ash. Both the PCDD and PCDF

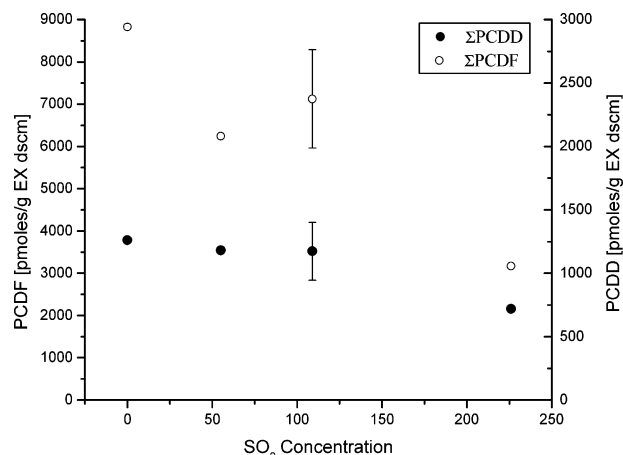


FIGURE 2. Effect of SO₂ concentration on total PCDD and PCDF emissions at 400 °C.

emissions decreased by up to a factor of 2.8 with increasing gas-phase SO₂ addition (see Figure 2). As the SO₂ concentration was increased at constant Cl₂, the emissions of PCDDs and PCDFs approached the emissions without the addition of gas-phase Cl₂ (run 1A-1). The decrease in PCDFs was consistently 1.5 times greater than that of PCDD. The changes to the homologue profiles due to SO₂ addition were minor compared to that observed from the addition of Cl₂ compared to the baseline test (without Cl₂), although these changes as noted by the degree of chlorination are well outside the coefficient of variance (CV) expected from replicate experiments. The triplicate runs at ~107 ppm SO₂ (runs 3A-1, 10A-1, and 11A-1) showed excellent reproducibility of the system, with CVs of 22 and 26% for the PCDD and PCDF emissions, respectively. The CVs for the degree of chlorination are 2% for the PCDDs and 3% for the PCDFs.

TABLE 2. Online Measurements of SO₂, HCl, and H₂O in the EFR at 400 °C^a

	test 1		test 2		test 3		test 4 (w/EX ash)		test 5 (w/EX ash)	
	inlet	outlet	inlet	outlet	inlet	outlet	inlet	outlet	inlet	outlet
SO ₂ [ppm]	0	0	110	76	105	55	0	0	105	15
Cl ₂ [ppm]	112	nm ^b	0	nm ^b	106	nm ^b	109	nm ^b	106	nm ^b
HCl [ppm]	0	45	0	6	0	64	0	88	0	218
H ₂ O [%]	0	8.4	0	8.4	0	8.5	0	8.7	0	8.4

^a All tests with Cl₂ and/or SO₂ added through port B (postcombustion, 400 °C). ^b nm: not measured.

The addition of SO₂ to the flue gas therefore affected both PCDD and PCDF emissions, albeit to a different degree. The relatively minor changes in the homologue profiles, degree of chlorination, and the consistency of the isomer profiles for each homologue (not shown) during the addition of SO₂ suggests that the responses of both the total PCDD/F and TEQ emissions are congruent; there is a decrease in total PCDDs/Fs and not just a shift to lower chlorinated or non-2,3,7,8-position substituted congeners (non-TEQ contributing). From these results, we can conclude that the addition of SO₂ affects a reaction pathway that has equal applicability to all homologues, regardless of the degree of chlorination. However, the PCDFs are more dependent upon this pathway(s) than the PCDDs. Ogawa et al. (21) also reported a greater effect of SO₂ on PCDF reduction than on that of PCDD in their fluidized bed combustor experiments.

Investigation of the SO₂/Cl₂ Interaction Relating to HCl and PCDD/F Formation. Prior work with EX fly ash in the EFR showed a dependency of the PCDD/F emissions on the gas-phase Cl₂ concentration (0–200 ppm); PCDF had a greater dependency as noted by a larger slope in the linear fit (19). The similarities between the influence of gas-phase Cl₂ on PCDD/F emissions and the addition of SO₂ (in the presence of Cl₂) might be consistent with theories suggesting an interaction between SO₂ and Cl₂, homogeneous or heterogeneous, resulting in the observed diminished emissions with increasing flue gas SO₂/Cl₂ ratios.

In order to evaluate the extent of the homogeneous reaction (R1) in the postcombustion zone at 400 °C, the reaction of SO₂ and Cl₂ in the EFR was investigated by measuring real-time changes in the HCl, H₂O, and SO₂ concentrations in the absence of PCDD/F sampling. Without the addition of SO₂ or fly ash (Table 2, test 1), 20% of the added Cl₂ was converted to HCl in the ethylene flame combustion gas ($\Phi = 1.33$) at 400 °C over the 1.3 s residence time. With the addition of SO₂ (test 3), a 10% increase in the conversion of Cl₂ and a 17% decrease in SO₂ over the respective base cases was observed. The respective changes might be consistent with the stoichiometry of R1; however, these results suggest only a minor, if any, extent of R1 at 400 °C and are probably insufficient to account for the extent of PCDD/F reduction.

The minor extent of reaction for R1 appears consistent with the results of other studies that did not observe homogeneous conversion of Cl₂ to HCl and depletion of SO₂ (15) or formation of SO₃ (12) below at least 750 °C. Minor differences in the extent of these reactions between the studies mentioned above and the present results may be due to persistent catalytic activity (see below) in the EFR after fly ash feeding experiments despite rigorous cleaning. These results suggest that R1 is not mainly responsible for the reduction in PCDD/F emissions. For example, a 10% decrease in the concentration of Cl₂ would be expected to result in a decrease in PCDF by approximately 8% (based on Wikström et al.) (19); the PCDF reduction in the present study was 41% when equivalent amounts of SO₂ and Cl₂ were added.

The postcombustion zone typically contains a relatively high concentration of fly ash; thus, the potential importance

of fly ash on the conversion of gas-phase Cl₂ to HCl (i.e., a heterogeneous reaction pathway) in the lower temperature regime was investigated. During EX fly ash injection into the combustion gas (400 °C) in the absence of SO₂, the HCl concentration doubled over the base case due to the addition of the fly ash (Table 2, test 1 vs test 4) with Cl₂ addition. With the addition of SO₂ and Cl₂ (test 5), the HCl concentration further increased to almost complete conversion of Cl₂ (based on the input concentration), and the exit concentration of SO₂ decreased by an additional 40 ppm (test 3 vs test 5). The conversion of SO₂ (test 2 vs test 5) and formation of HCl (test 4 vs test 5) due to added SO₂ in the presence of fly ash yields a ratio of HCl formation to SO₂ conversion of just over 2:1. Although this ratio is consistent with the stoichiometry of R1, fly ash was necessary at 400 °C, suggesting a heterogeneous reaction mechanism.

One possibility may be the formation of metal sulfates from metal chlorides in the fly ash, thus liberating HCl, as proposed by Gullett (22). In support of this reaction, Hunsinger et al. (8) observed that high levels of SO₂ in the flue gas led to significant decreases in chloride concentration (from 200 mg/g to <3 mg/g) of MSW incinerator fly ash. The HCl concentration was reported to increase consistent with the decrease in fly ash chloride. A shift from metal chlorides to metal sulfates in fly ash in the presence of high SO₂ has also been reported by Chen et al. (23). The observed increase in HCl in the present work could, therefore, be independent of any effect on the Deacon process and more related to the reduced concentration of metal chlorides within the fly ash. In addition to the insignificance of R1 in the postcombustion zone, this conclusion may also be consistent with the findings of Gullett et al. (12) in which CuSO₄ and CuO both produced Cl₂ via the Deacon process, albeit with somewhat different temperature behaviors.

If all of the chloride in the EX fly ash (5.7%) was released from the ash as HCl, a concentration of 55 ppm would have been expected. Thus, conversion of metal chlorides to metal sulfates cannot explain the entire observed HCl increase unless new metal chlorides were formed via the gas-phase Cl₂. To understand whether formation of metal chlorides could occur within the de novo temperature window, a metal oxide mixture (0.2 wt % CuO, 1.1 wt % Fe₂O₃, and bulk SiO₂) was treated with 100 ppm Cl₂ in 10% O₂/8% H₂O/N₂ at 300 °C. Due to the volatility of the copper and iron chlorides at typical PCDD/F formation temperatures and the absence of carbon in these experiments (to adsorb these metal chlorides), 300 °C was used for these fixed bed experiments instead of the 400 °C used elsewhere in this study. Evidence for volatilization of iron compounds during the treatment was observed by incomplete iron mass balances on samples exposed to Cl₂. An increase in the chloride content in the mixture after treatment with Cl₂ was observed via XRF analysis; a total of 16 mg/g was measured after 30 min of exposure compared to nondetectable pre-exposure concentrations. When the Cl₂ was replaced with 100 ppm of SO₂, no detectable increase in sulfates in the mixture could be discerned. Therefore, metal sulfates in the form of copper and iron do not form in the absence of Cl₂ at 300 °C. However,

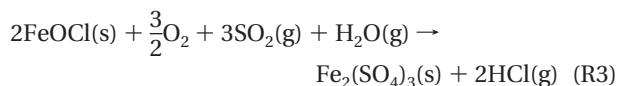
when both Cl₂ and SO₂ were added to the gas flow, both at 100 ppm, only 4.6 mg of chloride was measured in the treated mixture. The sulfate concentration increased to 21 mg/g. Therefore, the formation of metal chlorides can occur by the reaction of Cl₂ with metal oxides present in fly ash; metal chlorides can then be converted to metal sulfates in the presence of SO₂, within the PCDD/F formation temperature window.

For metal oxide conversion to metal chlorides, Saeki (24) reported that iron oxide can react with Cl₂ as follows

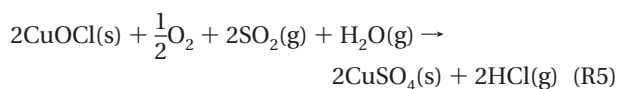


and this conversion is discussed related to PCDD/F formation by Ryan (25). An analogous reaction can likely occur with HCl, albeit to a lesser degree.

SO₂ may then react with FeOCl to generate the more stable, and perhaps less active, PCDD/F promoter, Fe₂(SO₄)₃:



Analogous reactions for CuO may also be postulated as



The conversion of copper and iron chlorides to sulfates, perhaps via R3 and R5, respectively, may significantly reduce or inhibit PCDD/F formation via the de novo synthesis. Since the de novo synthesis has been repeatedly concluded to be a main pathway for PCDF formation, and only partly responsible for PCDD formation (26, 27), the observed difference in behavior of PCDF and PCDD due to flue gas SO₂ might thus be explained. Metal sulfates, unlike specific metal chlorides, are not likely to be able to promote the formation of PCDD/F via the chlorination and partial oxidation of particulate carbon (de novo synthesis) and possibly PAHs; the formation of PCDDs/Fs from many PAHs has been reported by Wilhelm et al. (28). With regard to PCDDs, although Gullett et al. (12) did report a decrease in the conversion of PCDDs from phenol when replacing metal oxides with sulfates in the catalyst bed (e.g., surface-mediated condensation reactions), the reduction was relatively minor at the temperature of maximum observed conversion (400 °C, also the temperature of the current study). Thus, PCDD formation may be less affected by conversions such as those proposed in R3 and R5. The conversion to metal sulfates may not be inhibiting biaryl condensation to the same degree as it is inhibiting particulate carbon (and PAH) chlorination/oxidation steps required for the de novo synthesis.

Effect of SO₂/Cl₂ Addition and Reaction Temperature on PCDD/F Emissions. The relevance of R1 at high temperature was studied by injecting Cl₂ and SO₂ into the flame zone (port A). Adding 111 ppm of Cl₂ into combustion gas (without SO₂) in the flame zone (1000 °C) resulted in an HCl concentration of 212 ppm, virtually eliminating or at least significantly reducing the concentration of Cl₂ as a PCDD/F participant in the postcombustion zone. These conversion results are in agreement with Telfer (15). The addition of 109 ppm SO₂ into the flame zone (port A) with the Cl₂ increased the HCl concentration to 244 ppm and decreased the SO₂ concentration by 63% (to 40 ppm) with H₂O constant at 9.0%. Thus, at the high temperature, SO₂ addition is not necessary to achieve a very high conversion (>95%) of Cl₂ to HCl, but

TABLE 3. Effect of Location of Cl₂/SO₂ Addition on PCDD and PCDF Emissions

Run	port of addition		emissions (pmoles/g _{EX} dscm)					
	Cl ₂	SO ₂	mono-TriCDD	tetra-OctaCDD	total PCDD	mono-TriCDF	tetra-OctaCDF	total PCDF
2A-1	B	none	372	888	1261	4420	4407	8827
3A-1	B	B	346	564	910	2725	2457	5183
6A-1	A	none	360	496	855	3330	2281	5611
6A-2	A	none	363	611	973	2605	2947	5552
7A-1	A	A	371	354	725	3917	1389	5306
8A-1	B	A	324	539	863	3012	2088	5100
9A-1	A	B	460	411	870	3917	1995	5912

the addition of SO₂ could still contribute to the overall conversion (i.e., via R1).

To determine if the conversion of Cl₂ to HCl at high temperature can influence the formation of PCDD/F in the postcombustion zone, experiments 6–9 (see Table 1) were completed using port A (in combination with port B). The PCDD/F emissions decreased by approximately 30% when Cl₂ was added into the flame compared to addition directly into the postcombustion zone, both in the absence of added flue gas SO₂ (cf. Table 1, runs 6A-1 and 6A-2 vs run 2A-1). A very slight shift to a lower degree of chlorination might have been observed in run 6A-1, due to an observed increase in MoCDFs-TriCDFs and decrease in TeCDFs-OCDFs. However, this decrease was not consistent with the replicate run (run 6A-2). The reduced amount of Cl₂ due to conversion to HCl at high-temperature could explain the reduced emissions and minute effects on the homologue profile, as discussed previously, since HCl may be inactive for PCDD/F formation (19) or at least less active than Cl₂ (29).

When SO₂ was also added into the flame zone, the high temperature may have enhanced the conversion of the minute amount of remaining Cl₂ to HCl via R1. While the overall PCDD/F emissions were not reduced, a definite shift in the homologue pattern did occur (unlike the minor, if any, changes noted above). The tetra- thru octachlorinated emissions were considerably lower, resulting in a reduction in the TEQ by 60%. A 35% reduction in TeCDD-OCDD and a 47% reduction in TeCDF-OCDF emissions can be seen in Table 3 (see runs 6A-1 and 6A-2 with run 7A-1). The reduction in PCDD TEQ was 49%, while the reduction in PCDF TEQ was 70%; this again reflects the more pronounced influence of SO₂ addition on PCDFs compared to PCDDs.

To understand if the high-temperature reaction between SO₂ and the ethylene flame products could be responsible for the above results via formation of sulfur analogues to PCDD/F precursors, Cl₂ was added through port B while SO₂ was added through port A. Therefore, the SO₂ contacted the flame products in the combustion zone, while the Cl₂ did likewise only in the postcombustion zone (400 °C). The results, however, were similar to when both components were added to the postcombustion zone; the total PCDD and PCDF emissions were reduced with little change in the degree of chlorination (see Table 1) or homologue profile (Table 3). Since the interaction temperature of the Cl₂/SO₂/fly ash (400 °C) was not changed by the addition of only SO₂ at port A, and high concentrations of Cl₂ were again present in the postcombustion zone, the results were expected to be in agreement with those from the port B Cl₂/SO₂ addition experiments. These results do confirm that any potential high-temperature homogeneous reactions of SO₂ with the flame products do not contribute to reduced PCDD/F emissions.

Conversely to the above experiment, when Cl₂ was added through the combustion zone (port A) and SO₂ through the postcombustion zone (port B), the results were now similar to those observed when both SO₂ and Cl₂ were added into

the combustion zone in terms of both homologue profile changes and emissions (Table 3). Although a slight difference might be noticed (run 7A-1 vs run 9A-1), these changes may well be within the range of the reproducibility of the experiments. One explanation could be that the high temperature interaction of SO₂ and Cl₂ according to R1 has a similar net effect on the homologue profile (and TEQ) as that of SO₂/Cl₂ (or HCl)/fly ash interaction at lower temperature. Alternatively, and more likely, the effect may be due entirely to the latter (heterogeneous reactions), as will be discussed below.

Effect of SO₂ on PCDD/F Emissions in the Absence of Combustion Gas. The results discussed so far have supported a conclusion that the homogeneous reaction R1 is not a major reason for the reduction in PCDD/F due to the addition of SO₂ in the flue gas. Therefore, the reduction should not be related to the presence of water vapor in the flue gas necessary for R1 to proceed. To further show that SO₂ can have an effect on PCDD/F emissions independent of R1 and water vapor, EX fly ash experiments in a dry air (no flame) atmosphere were performed (runs 12A-1, 13A-1, and 20A-1). Without the ethylene combustion products (e.g., organics and H₂O) and SO₂, PCDF emissions were significantly lower than during the presence of the nonsooting flame; PCDD emissions, however, actually increased (Table 1, run 2A-1 and 12A-1). Without the H₂O from the flame present, the degree of chlorination increased sharply, in agreement with the findings of Wikström (17). These results suggest the role of flame products (e.g., PAHs) in PCDF formation, in addition to the particulate carbon in the EX fly ash, and a competition with reaction pathways for PCDDs. In support of this competition, Briois et al. (30) reported a decrease in the yield of PCDDs from a mixture of chlorophenols passed over an oxidized fly ash when water vapor was added to the reactor gas flow.

The addition of 107 ppm SO₂ to the no flame case (with added Cl₂) resulted in an apparent reduction in the PCDF emissions by 28% and no discernible difference in the PCDD emissions (Table 1, run 13A-1), without affecting the degree of chlorination. Doubling the SO₂ concentration did not result in a further decrease in total PCDF (Table 1, run 20A-1); however, the increase in SO₂ concentration did significantly affect the homologue distribution (i.e., lower degree of chlorination). Only a minor reduction in PCDD might have occurred with a minor change in the homologue profile, although this reduction may be within the expected experimental variance.

The results suggest that SO₂ can have an impact on PCDD/F formation without the potential for R1 (i.e., no water vapor). Since the Deacon process is not necessary to produce Cl₂ in this situation (excess Cl₂ added), the influence of SO₂ under these conditions is most likely not on this process. The relatively minor impact on PCDDs also suggests that the effect of SO₂ addition was not on the catalyst activity related to biaryl condensation reactions or that such reactions are not responsible for the bulk of PCDD formation. Overall, these results add support to the conclusion that the SO₂ interaction with metal chlorides may be the predominant inhibition mechanism, perhaps according to R2/R3 or R4/R5.

Influence of SO₂ Addition on PCDD/F Emissions during Poor Combustion. Periods of unstable combustor operation, such as during startup and shutdown, have been related to increased PCDD/F emissions (8, 31, 32). The increase in sooting during these phases has been suggested as a possible reason for increased emissions even many hours after returning to normal operation (memory effect) (27, 31, 33–35). Such “sooty” combustion has led to orders of magnitude increases in PCDD/F emissions in laboratory studies over baseline cases (no flame and nonsooting flames) (20,

TABLE 4. Effect of Equivalence Ratio and SO₂ Addition of PCDD and PCDF Emissions

run	port B addition (ppm)		emissions (pmoles/g _{EX} dscm)			
	Cl ₂	SO ₂	penta- OctaCDD	total PCDD	penta- OctaCDF	total PCDF
2A-1	109	none	705	1261	2484	8827
3A-1	109	109	438	910	1359	5183
14A-2	119	none	1322	2115	17761	37904
15A-1	119	109	1089	1805	3065	12096
16A-1	119	109	1094	1590	2673	5513

34). Due to the potential importance of sooting to the global PCDD/F burden, this study was extended to investigate the effect of SO₂ addition during sooty combustion (runs 14A-2, 15A-1, and 15A-2). At $\Phi = 1.87$, the premixed ethylene/air torch-type burner reproducibly produced soot [based on the smoke test (36)]; soot inception occurred at around $\Phi = 1.79$. With ~2 g of fly ash added to the system over a period of 2 h, an independent mass measurement of the amount of soot produced and collected was not possible. In the absence of SO₂, the total PCDF and PCDD emissions were 4.3 and 1.7 times greater, respectively, than the emissions during the nonsooting flame. It must be noted that quantification of all TeCDD, some DiCDF, and some TeCDF isomers was not possible for the sooting experiments due to large interferences. For run 15A-2, all TriCDFs were lost due to such interferences. However, comparison of the penta- to octa-CDDs/Fs for runs 15A-1 and 15A-2, run under the same conditions, shows excellent repeatability (see Table 4).

When SO₂ was added to the system postflame zone (port B), 68 and 15% reductions in PCDF and PCDD, respectively, occurred in run 15A-1. Similar decreases, comparing the PeCDD/F–OCDDs/Fs only (due to the interferences), were observed in run 15A-2 as well. The reduction in PCDF emissions was somewhat higher during the sooting combustion when compared to the nonsooting combustion test (68 vs 41%). However, the reduction in PCDD emissions was somewhat higher during the nonsooting combustion (15 vs 21%). The findings suggest that increasing the SO₂ concentration in the flue gas during periods of poor combustion (e.g., coal/MSW cofeeding during transient periods) can reduce PCDD/F emissions.

Mechanistic Understanding of the Effect of SO₂ on PCDD/F Formation. The present work has shown that R1 is not a major reason for the reduction in PCDD/F under the conditions tested. The experimental results also suggest that reductions in PCDD/F formation/reduction happen primarily independently from the Deacon process, suggesting that either the influence of SO₂ is minimal on the copper catalyst at the temperature studied or that the Deacon process is not a major part of the PCDD/F formation process under these experimental conditions. Metal sulfates (copper or iron) were only detected via XRF analysis when Cl₂ and SO₂ were added into the gas together (at 300 °C) in the present study. The results suggest that the reduction in PCDD/F due to SO₂ addition is likely a result of the heterogeneous interaction of metals in the fly ash with HCl/Cl₂ to form metal chlorides (e.g., via R2 and R4) and (subsequently) SO₂ to form metal sulfates (e.g., via R3 and R5). While copper and iron chlorides have been extensively shown to promote PCDD/F formation, their analogous sulfates do not.

Investigation of Potential Memory Effects of SO₂ Addition in the EFR. The above conclusions are in agreement with the findings of Hunsinger et al. (8) in which they concluded that PCDD/F formation in MSW incineration is due primarily to ash deposits. Altwickler (37) postulated that wall deposits in incinerators could be a major source and that continual renewal of deposits would be important when

comparing lab-scale (fixed bed) experiments and full-scale incinerator sampling. The formation of metal sulfates replacing metal chlorides, albeit proposed at higher temperatures within the incinerator, were concluded to lead to reduced emissions from downstream fly ash deposits during the feeding of SO₂ (8). The objective of the B runs in the present work was to evaluate the potential memory effect of SO₂ addition on PCDD/F emissions from such deposits in the laboratory-scale flow reactor.

The B runs were sampled after the conclusion of the A runs; there was no SO₂ addition during any B run, although the Cl₂ addition was continued. No additional fly ash was fed during the B runs, with the exception of runs 10 and 11. After fly ash feeding (during the A runs), an average of 25% of the fly ash fed remained in the vertical reactor attached to the walls. This ash remains reactive, forming PCDDs/Fs for hours after cessation of fly ash feeding (27, 38). Comparison of runs 2B-1 and 6B-1 to their corresponding A segments indicates that residual PCDD and PCDF emissions from the wall fly ash were approximately 4% of that during fly ash feeding, on a pmoles/g_{EX} (fed) dscm basis. Converting to a pmoles/g_{EX} (deposit) dscm basis, the residual emissions from the wall deposits were between 20 and 30% of that during the fly ash feeding. A reduction in formation on fly ash or soot/fly ash with time has been reported previously (27, 39–41). The rate of decrease in PCDD/F formation with time is a strong function of the reaction temperature; net formation at 300 °C persists, relative to its initial formation, longer than at higher temperature (41).

The addition of SO₂ during the A run appeared to lower the emissions detected from the B runs (see Table 1). When fly ash feeding was resumed (11B-1), the emissions returned to their pre-SO₂ addition concentrations. These results, in general, suggest that SO₂ can have a lasting effect on the ability of the fly ash to promote PCDD/F formation; this observation is perhaps consistent with the pilot-scale findings of Hunsinger (8). Both Gullett et al. (42) and Lindbauer et al. (3) have reported observing a memory effect of coal cofeeding in MSW incineration. However, fresh deposits formed in the absence of SO₂ appear to have greater activity than “aged” deposits (contribute more to the PCDD/F emissions) (43), thus potentially reducing or eliminating the potential SO₂ memory effect.

The time scale for reduction of the memory effect of high-sulfur fuels may be facility or feed dependent, as Hunsinger et al. (8) report increased PCDD/F emissions shortly after cessation of the SO₂ feed on a pilot scale incinerator. The authors further note that the effects of SO₂ addition on PCDD/F emissions are delayed by up to several hours due to residual activity of fly ash deposits (formed without high SO₂ flue gas concentrations) and a diffusion limitation of SO₂ to these deposits. These observations further support the heterogeneous reaction theory suggested herein related to the reduction in PCDD/F due to low flue gas Cl₂ (or HCl)/SO₂ ratios. Fly ash deposits, with chloride to sulfate ratios directly related to the Cl/S flue gas ratio, will continually be formed and are important for PCDD/F emissions. The composition of the ash, chlorides versus sulfates, is most likely directly related to the PCDD/F emissions; the “age” of the ash deposits is also an important parameter. More work in understanding the relationship between metal salt chemistry in combustion flue gas related to PCDD/F formation (specifically, chlorination and particulate carbon oxidation) would further aid in the development of the kinetic mechanism describing PCDD and PCDF emissions in incineration.

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Literature Cited

- (1) Xu, X.; Li, X.-d.; Yan, J.-h.; Lu, S.-y.; Gu, Y.-l.; Chi, Y.; Cen, K.-f. PCDD/Fs emission in a 150 t/d MSW and coal co-firing fluidized bed incinerator. *J. Zhejiang Univ.* **2001**, 2 (3), 278–283.
- (2) Lu, S.-Y. Mechanistic and experimental study on PCDD/Fs formation, emission and control during solid waste and coal combustion process. Zhejiang University, 2004.
- (3) Lindbauer, R. L.; Wurst, F.; Prey, T. Combustion dioxin suppression in municipal solid waste incineration with sulfur additives. *Chemosphere* **1992**, 25 (7–10), 1409–1414.
- (4) Skodras, G.; Grammelis, P.; Samaras, P.; Vourliotis, P.; Kakaras, E.; Sakellariopoulos, G. P. Emissions monitoring during coal waste wood co-combustion in an industrial steam boiler. *Fuel* **2002**, 81, 547–554.
- (5) Gullett, B. K.; Raghunathan, K.; Dunn, J. E. The effect of cofiring high-sulfur coal with municipal waste on formation of polychlorinated dibenzodioxin and polychlorinated dibenzofuran. *Environ. Eng. Sci.* **1998**, 15, 59–69.
- (6) Gullett, B. K.; Raghunathan, K. Observations on the effect of process parameters on dioxin/furan yield in municipal waste and coal systems. *Chemosphere* **1997**, 34 (5–7), 1027–1032.
- (7) Gullett, B. K.; Dunn, J. E.; Bae, S.-K.; Raghunathan, K. Effects of combustion parameters on polychlorinated dibenzodioxin and dibenzofuran homologue profiles from municipal waste and coal co-combustion. *Waste Manage.* **1998**, 18, 473–483.
- (8) Hunsinger, H.; Song, G. J.; Seifert, H.; Jay, K. Influence of SO₂ on the formation of PCDD/F in MSWI. *3rd i-CIPEC Conference*; Hangzhou, China, 2004; pp 300–306.
- (9) Palladas, A.; Samaras, P.; Sakellariopoulos, G. The effect of sulfur on the inhibition of PCDD/F formation during co-combustion of coal and solid waste. *Organohalogen Compd.* **2004**, 66, 1250–1256.
- (10) Griffin, R. A new theory of dioxin formation in municipal waste combustion. *Chemosphere* **1986**, 15 (9–12), 1987–1989.
- (11) Bruce, K. R.; Beach, L. O.; Gullett, B. K. The role of gas-phase Cl₂ in the formation of PCDD/PCDF during waste combustion. *Waste Manage.* **1991**, 11, 97–102.
- (12) Gullett, B. K.; Bruce, K. R.; Beach, L. O. Effect of sulfur dioxide on the formation mechanism of polychlorinated dibenzodioxin and dibenzofuran in municipal waste combustors. *Environ. Sci. Technol.* **1992**, 26 (10), 1938–1943.
- (13) Buser, H. R. Identification and sources of dioxin-like compounds: I. polychlorodibenzothiophenes and polychlorodibenzofurans, the sulfur-analogues of the polychlorodibenzofurans and polychlorodibenzodioxins. *Chemosphere* **1992**, 25 (1–2), 45–48.
- (14) Raghunathan, K.; Gullett, B. K. Role of sulfur in reducing PCDD and PCDF formation. *Environ. Sci. Technol.* **1996**, 30 (6), 1827–1834.
- (15) Telfer, M.; Gullett, B. K. Experimental investigations of homogeneous gas-phase SO₂ and Cl₂ reactions for PCDD/F suppression. *Organohalogen Compd.* **2002**, 56, 353–356.
- (16) Bechtler, R.; Stieglitz, L.; Zwick, G.; Will, R.; Roth, W.; Hedwig, K. Influence of elemental sulfur on the de-novo-synthesis of organochlorine compounds from residual carbon on fly ash. *Chemosphere* **1998**, 37 (9–12), 2261–2278.
- (17) Wikström, E.; Ryan, S.; Touati, A.; Gullett, B. K. Key parameters for de novo formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans. *Environ. Sci. Technol.* **2003**, 37 (9), 1962–1970.
- (18) Glassman, I. *Combustion*, 2nd ed.; Academic Press: New York, 1987; Chapter 8: Environmental combustion considerations, pp 318–385.
- (19) Wikström, E.; Ryan, S. P.; Touati, A.; Telfer, M.; Tabor, D.; Gullett, B. K. Importance of chlorine speciation on de novo formation of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans. *Environ. Sci. Technol.* **2003**, 37 (6), 1108–1113.
- (20) Wikström, E.; Ryan, S.; Touati, A.; Tabor, D.; Gullett, B. K. The origin of carbon in polychlorinated dioxins and furans formed during sooting combustion. *Environ. Sci. Technol.* **2004**, 38 (13), 3778–3784.
- (21) Ogawa, H.; Orita, N.; Horaguchi, M.; Suzuki, T.; Okada, M.; Yasuda, S. Dioxin reduction by sulfur component addition. *Chemosphere* **1996**, 32 (1), 151–157.

- (22) Gullett, B. K. Dioxin formation mechanisms: implications for combustion technologies. *2nd Asia Pacific Conference on Sustainable Energy and Environmental Technologies*; Gold Coast, Australia, 1998.
- (23) Chen, J.-C.; Wy, M.-Y.; Yan, M.-H. Theoretical and experimental study of metal capture during incineration process. *J. Environ. Eng.* **1997**, *123* (11), 1100–1106.
- (24) Saeki, Y.; Matsuzaki, R.; Fujiwara, S. Reaction process between iron(II) chloride and oxygen. *Bull. Chem. Soc. Jpn.* **1978**, *51* (12), 3527–3529.
- (25) Ryan, S. P. *The formation of polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/F) via the de novo synthesis in the catalytic extraction process (CEP) and the role of iron chloride*; Rensselaer Polytechnic Institute: 2001.
- (26) Hell, K.; Stieglitz, L.; Dinjus, E. Mechanistic aspects of the de-novo synthesis of PCDD/PCDF on model mixtures and MSWI fly ashes using amorphous ¹²C- and ¹³C-labeled carbon. *Environ. Sci. Technol.* **2001**, *35* (19), 3892–3898.
- (27) Wikström, E.; Ryan, S.; Touati, A.; Gullett, B. K. *in situ* formed soot deposits as a carbon source for polychlorinated dibenzo-p-dioxins and dibenzofurans. *Environ. Sci. Technol.* **2004**, *38* (7), 2097–2101.
- (28) Wilhelm, J.; Stieglitz, L.; Dinjus, E.; Will, R. Mechanistic studies of the role of PAHs and related compounds in PCDD/F formation on model fly ashes. *Chemosphere* **2001**, *42*, 797–802.
- (29) Addink, R.; Bakker, W. C. M.; Olie, K. Influence of HCl and Cl₂ on the formation of polychlorinated dibenzo-p-dioxins/dibenzofurans in a carbon/fly ash mixture. *Environ. Sci. Technol.* **1995**, *29* (9), 2055–2058.
- (30) Briois, C.; Gullett, B. K.; Ryan, S. P.; Tabor, D.; Clayton, M.; Touati, A. Dioxin and furan formation on fly ash from a mixture of chlorophenols *Organohalogen Compd.* **2005**, *67*, 2215–2218.
- (31) Gass, H. C.; Luder, K.; Wilkin, M. PCDD/F emissions during cold start-up and shut-down of a municipal waste incinerator. *Organohalogen Compd.* **2002**, *56*, 193–196.
- (32) Grosso, M.; Cernuschi, S.; Palini, E.; Lodi, M.; Mariano, G. PCDD/Fs release during normal and transient operation of a full scale MSWI plant. *Organohalogen Compd.* **2004**, *66*, 1243–1249.
- (33) Addink, R.; Altwicker, E. R. Formation of polychlorinated dibenzo-p-dioxins and dibenzofurans from chlorinated soot. *Carbon* **2004**, *42* (12–13), 2661–2668.
- (34) Ryan, S.; Wikström, E.; Gullett, B. K.; Touati, A. Investigation of the pathways to PCDDs/Fs from an ethylene diffusion flame: formation from soot and aromatics. *Organohalogen Compd.* **2004**, *66*, 1119–1125.
- (35) Zimmermann, R.; Blumenstock, M.; Heger, H. J.; Schramm, K. W.; Kettrup, A. Emission of nonchlorinated and chlorinated aromatics in the flue gas of incineration plants during and after transient disturbances of combustion conditions: delayed emission effects. *Environ. Sci. Technol.* **2001**, *35* (6), 1019–1030.
- (36) Kent, J. H. A quantitative relationship between soot yield and smoke point measurements. *Combust. Flame* **1986**, *63*, 349–358.
- (37) Altwicker, E. R. Some laboratory experimental designs for obtaining dynamic property data on dioxins. *Sci. Total Environ.* **1991**, *104*, 47–72.
- (38) Ueno, S.; Nishino, J.; Yoshihara, S.; Weber, R. PCDD/PCDF memory effects in a laboratory scale incinerator. *Organohalogen Compd.* **2002**, *56*, 177–180.
- (39) Stieglitz, L.; Vogg, H. On formation conditions of PCDD/PCDF in fly ash from municipal waste incinerators. *Chemosphere* **1987**, *16* (8/9), 1917–1922.
- (40) Addink, R.; Drijver, D.; Olie, K. Formation of polychlorinated dibenzo-p-dioxins/dibenzofurans in the carbon/fly ash system. *Chemosphere* **1991**, *23*, 1205–1211.
- (41) Ryan, S.; Altwicker, E. R. Understanding the role of iron chlorides in the de novo synthesis of polychlorinated dibenzo-p-dioxins/dibenzofurans. *Environ. Sci. Technol.* **2004**, *38* (6), 1708–1717.
- (42) Gullett, B. K.; Dunn, J. E.; Raghunathan, K. Effect of cofiring coal on formation of polychlorinated dibenzo-p-dioxins and dibenzofurans during waste combustion. *Environ. Sci. Technol.* **2000**, *34* (2), 282–290.
- (43) Lee, C. W.; Kilgroe, J. D.; Raghunathan, K. Effect of soot and copper combustor deposits on dioxin emissions. *Environ. Eng. Sci.* **1998**, *15* (1), 71–84.

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