

Role of Sulfur in Reducing PCDD and PCDF Formation

K. RAGHUNATHAN

Acurex Environmental Corporation, 4915 Prospectus Drive,
P.O. Box 13109, Research Triangle Park, North Carolina 27709

BRIAN K. GULLETT*

Air Pollution Prevention and Control Division, U.S.
Environmental Protection Agency, MD-65, Research Triangle
Park, North Carolina 27711

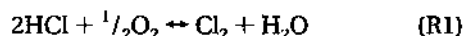
Past research has suggested that the presence of sulfur (S) in municipal waste combustors (MWCs) can decrease the downstream formation of chlorinated organic compounds, particularly polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Thus, co-firing a MWC with coal, because of the S species from coal, may reduce PCDD and PCDF emissions. Experiments were carried out to test this hypothesis and to determine the role of S. A field-sampled MWC fly ash was injected into the EPA's pilot-scale reactor, doped with hydrogen chloride (HCl). The tests involved either natural gas or coal combustion. Besides the combustion environment, MWC fly ash injection temperature and sulfur-to-chlorine ratio (S/Cl) were varied. Flue gas was sampled and analyzed for PCDD and PCDF to determine in-flight formation. In the natural-gas-fired reactor, when S was added (as sulfur dioxide, SO₂), the PCDD and PCDF formation decreased dramatically at S/Cl ratios as low as 0.64, and with varying furnace conditions, the inhibitory effect was consistent for S/Cl ratios of about 1. In tests with the coal-fired furnace, the S inhibitory effect was again observed at S/Cl values of 0.8 and 1.2, respectively, for the two coals tested. S inhibition mechanisms were studied in a bench-scale reactor. Results show that the depletion of molecular chlorine (Cl₂), an active chlorinating agent, by SO₂ through a gas-phase reaction appears to be a significant inhibition mechanism in addition to previously reported SO₂ deactivation of copper catalysts.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), even in trace amounts, are highly toxic. These compounds have been detected in the emissions of municipal and hazardous waste combustors on both the gaseous and particulate (fly ash) phases. Since they are formed at lower temperatures (250–400 °C) and

are chemically stable in general, a practical control strategy for reducing their emissions is to minimize their formation rather than to destroy or capture them after formation.

A number of studies have addressed PCDD and PCDF formation. Under laboratory conditions simulating a MWC post-furnace environment, experiments with MWC fly ash have shown substantial PCDD and PCDF formation (1). A theory has been proposed (2) and tested (3) that shows that formation occurs due to *de novo* synthesis from compounds within the flue gas and fly ash. This synthesis involves the Deacon process reaction

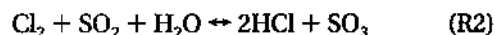


which is catalytically driven by the copper (Cu) species present in the fly ash. The Cl₂ produced subsequently chlorinates the aromatic ring structures through substitution reactions. A PCDD and PCDF source of chlorine (Cl) has been confirmed as Cl₂ (4), and the latter's derivation from primarily the Deacon process has been determined (5). It is suggested that the carbon source is derived from unburnt particulate matter (1) reacting with O₂ and Cl₂ to form PCDD and PCDF. An alternative theory suggests that the carbon source is derived from high-temperature radical reactions during combustion (6) that react at lower temperatures to form PCDD and PCDF (7, 8). This theory indicates the catalytic involvement of fly ash constituents in forming biaryl structures from chloroorganic compounds (7, 9). Thus, the catalytic properties of fly ash may be responsible for both the Cl₂ production and the biaryl synthesis. Concentrations of HCl (or Cl₂), organic precursors, and possibly Cu catalytic sites (10) are important parameters in PCDD and PCDF formation.

In contrast to MWCs, only small amounts of PCDD and PCDF were detected in the emissions from coal-fired combustors despite the presence of Cl and organic ring structures in both systems. Emissions sampling from a combined coal/municipal waste plant showed no detectable tetrachlorinated dibenzodioxin (TCDD), nor were noteworthy amounts found on coal fly ash (11). Co-firing of coal with refuse-derived fuel (RDF) also showed PCDD and PCDF below detection levels, in spite of increased HCl levels due to the RDF (12). However, laboratory studies of Mahle and Whiting (13) produced chlorodioxins in tests with bituminous coal.

A distinct difference between coal-fired utility power plants and MWCs is the higher levels of S species, or the S/Cl ratio, in the former. A typical S/Cl ratio in a MWC is about 0.2, which is an order of magnitude lower than that found in coal combustion. Recent work by Lindbauer et al. (14) has demonstrated that co-firing of coal in a municipal solid waste (MSW) incinerator leads to appreciably lower PCDD and PCDF levels. There are several possible mechanisms of interference by the S species:

(1) Griffin (2) suggested that the effect of S is to deplete the Cl₂ levels through the gas-phase reaction



thereby inhibiting the aromatic substitution reactions. Thus, a higher S/Cl ratio can discourage the chlorination step.

* Corresponding author telephone: (919)541-1534; fax: (919)541-0554; e-mail address: bgullett@engineer.aeer.epa.gov.

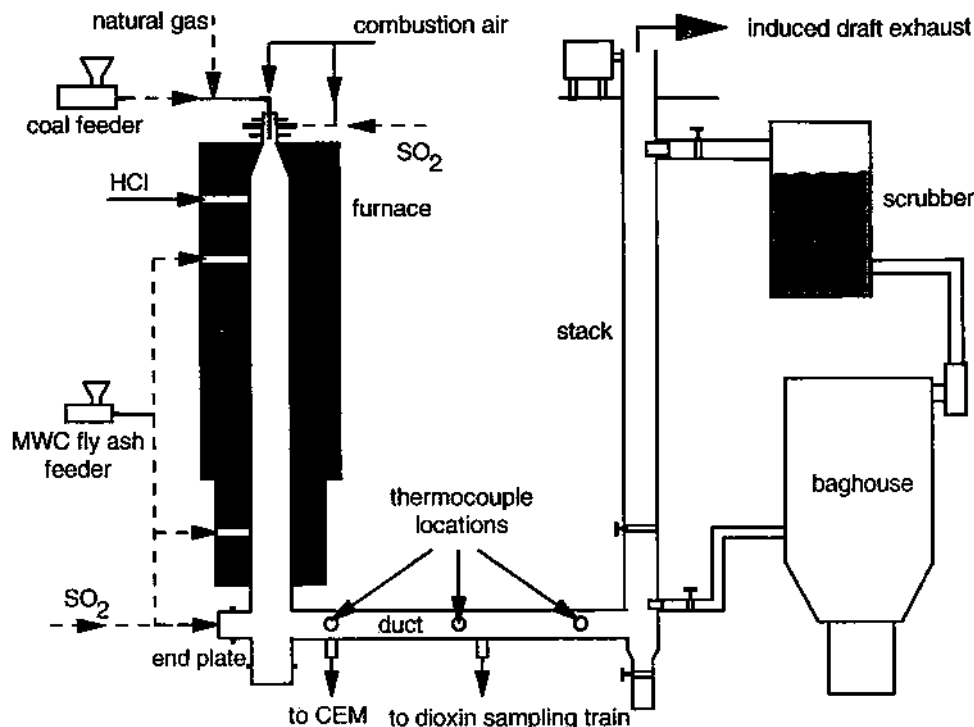


FIGURE 1. Schematic of the pilot-scale innovative furnace reactor (IFR).

(2) The role of S is to reduce the catalytic activity of the fly ash by reacting with the Cu-based Deacon catalyst in the fly ash (e.g., CuO) to form CuSO₄. Gullett et al. (15) have shown that, around the peak PCDD formation temperature of about 350 °C, CuSO₄ is a less active catalyst for the production of Cl₂ through the Deacon process as well as for the biaryl synthesis step of PCDD formation.

(3) The presence of SO₂ sulfonates the phenolic PCDD and PCDF precursors, preventing subsequent chlorination and biaryl synthesis. However, there is little information on this possible effect.

The possible difference in Cu concentrations between the coal- and MSW-fired processes does not seem to explain the difference in the PCDD and PCDF levels (15).

Thus, co-firing MWCs with coal would result in higher S levels, which may reduce PCDD and PCDF formation. Published work on the effects of sulfur in reducing formation is scarce. The importance of various S inhibition mechanisms, except for effects on fly ash catalytic activity (15), is not clear. This work demonstrates, through pilot-scale tests, that S species can reduce PCDD and PCDF yields substantially. Further insight into the inhibition mechanism is presented through bench-scale studies.

Experimental Procedures

The experimental systems used are (1) pilot-scale innovative furnace reactor (IFR) and (2) bench-scale chlorinated organics reactor (COR). These facilities are described briefly below.

Innovative Furnace Reactor (IFR). A schematic of the pilot-scale IFR setup is shown in Figure 1. The IFR is a down-fired, refractory-lined cylindrical unit with a length of about 3 m and an internal diameter (i.d.) of 15.2 cm, nominally rated at 29.3 kW. The last series of tests reported in this work were conducted after an IFR upgrade, which resulted in a 20.3 cm i.d. and a 48.8 kW firing rate, following replacement of refractories. The facility can be fired with either a gaseous fuel or pulverized coal. Ports along the

TABLE 1

Analysis of Coals Used (%)

	IBC-109	Pittsburgh no. 8
carbon	69.8	74.7
hydrogen	4.7	4.9
nitrogen	1.7	1.9
sulfur	1.1	2.6
chlorine	0.4	0.0
ash	7.5	7.5
oxygen	8.7	7.0
moisture	6.6	1.4
calorific value (kJ/kg)	31 425	31 884

length of the IFR facilitate the addition of reactants and sampling. The unique design of the furnace allows for staging of combustion to simulate various applications, including MSW combustion.

IFR tests involved either natural gas or coal. MWC conditions were simulated by re-injecting a MWC fly ash into the furnace and doping the furnace with HCl. SO₂ was doped into the furnace at varying rates to represent the S species from coal combustion. The coals used were an Illinois coal (IBC-109) and Pittsburgh no. 8 coal, injected into the IFR burner in a pulverized form. The analyses of the coals are given in Table 1. The MWC fly ash sample was from an electrostatic precipitator hopper on a full-scale mass-burn facility at Quebec City, Canada (16), prior to facility modifications for improved combustion, and Table 2 shows the analysis of the as-received fly ash. This fly ash was fed into the furnace by a K-Tron feeder at a nominal rate of 100 g/h, introduced through various IFR ports, representing different injection temperatures.

Flue gas from the duct was sampled for organics (PCDD and PCDF) using isokinetic sampling and EPA Modified Method 5 (MM5) sampling protocols. The sampling trains consisted of a quartz sampling probe, followed by a filter, XAD trap, and impingers. The probe rinse, filters, and XAD

TABLE 2

Analysis of Raw MWC Fly Ash Used (ng/g of Fly Ash)

congener	CBz	CPh	PCDD	PCDF
di	23	nm ^a	nm	nm
tri	25	nm	nm	nm
tetra	19	50	nd ^b	3.9
penta	15	100	nd	1.8
hexa	7	nm	1.2	1.0
hepta	nm	nm	1.7	0.9
octa	nm	nm	2.0	0.1
total	89	150	4.9	7.7

^a nm, not measured. ^b nd, none detected.

were analyzed together for tetra-octa-PCDD and -PCDF congeners.

Furnace emissions were also sampled from the duct section and then passed through heated sample lines to continuous emission monitors (CEMs) to measure the concentrations of SO₂, CO₂, O₂, CO, and NO_x. For some tests, the HCl concentration in the furnace was determined using the EPA Method 26 protocol.

IFR tests involved various phases, differing in the fuel type, firing rate, flue gas, and duct conditions; these parameters are summarized in Table 3. The reported PCDD and PCDF yields represent in-flight formation, with fly ash residence times in seconds. Note that these results represent only one measurement, and hence their significance is only qualitative.

Chlorinated Organics Reactor (COR). The COR facility was used previously for S-inhibition studies on PCDD formation (15), and its schematic is shown in Figure 2. The COR is a concentric tube, quartz reactor inserted into the horizontally mounted, single-zone, electric furnace. The COR was used in this work for mechanism studies, and two types of tests were performed. In both cases, the COR process gas was 10% O₂ in nitrogen (N₂), and the reactor outlet was connected to a TECO HCl analyzer to continuously record the HCl concentration.

One set of tests studied the homogeneous gas-phase reaction between Cl₂ and SO₂, and the COR schematic for these tests is shown in Figure 2a. Cl₂ and SO₂ were added to the process gas to yield inlet concentrations of 500 and 1000 ppm, respectively, resulting in a S/Cl (molar) ratio of 1. Part of the N₂ in the process gas was bubbled through a water column to yield a H₂O concentration of 3%. The COR was operated under these conditions for about 3 h; then the SO₂ was replaced by equivalent N₂ flow, and the test continued for 1 h. During the entire experiment, the

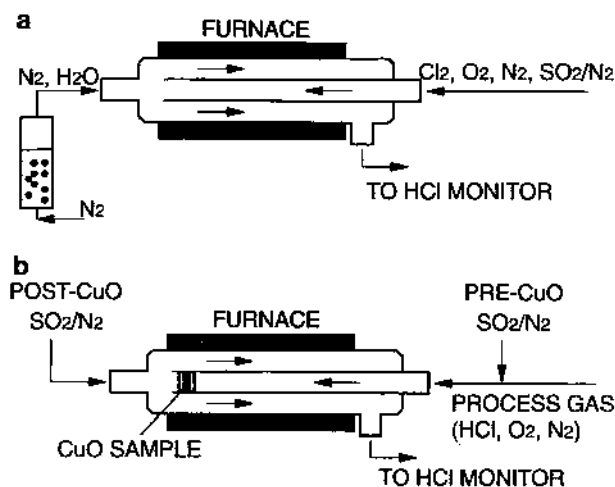


FIGURE 2. (a) Schematic of the chlorinated organics reactor (COR) setup for studying gas-phase reaction between SO₂ and Cl₂. (b) Schematic of the chlorinated organics reactor (COR) setup for comparison of SO₂ catalyst poisoning versus gas-phase chlorine depletion effects.

progress of the reaction was observed by continuously monitoring the HCl concentration at the reactor exit.

The second set of COR tests used CuO to simulate MWC fly ash catalytic properties. These COR tests were conducted in pairs to examine the relative effects of SO₂ between catalyst poisoning and depletion of gas-phase chlorine species. As depicted in Figure 2b, about 1 g of the solid sample was embedded in a quartz wool bed and placed near the end of the inner tube of the reactor; HCl was introduced from the right, into the inner tube, at 1000 ppm. In one test, SO₂ entered along with HCl and, hence, passed through the catalyst; in a companion test, SO₂ was introduced from the left, immediately after the catalyst. The reaction was monitored over 4 h, and SO₂ at 1000 ppm was introduced over a 60-min window during this period. Again, the HCl concentration in the COR effluent stream was continuously monitored. In these tests, the sample was pretreated in an inert (10% O₂) atmosphere at 400 °C for 30 min. The test temperature was also 400 °C.

Sample Analysis. IFR samples were analyzed in the EPA's in-house facilities by high-resolution gas chromatography/low-resolution mass spectrometry (HRGC/LRMS), using a Hewlett-Packard 5890/5970 gas chromatography/mass selective detector (GC/MSD). Details were reported elsewhere (17). The results obtained were levels of each tetra-octa-PCDD and -PCDF congener in the sample. In addition to the PCDD and PCDF congeners, the raw fly ash samples were also analyzed for chlorobenzenes (CBz) and chlorophenols (CPh). Table 2 also includes these results.

TABLE 3

Summary of Pilot-Scale Test Conditions

test phase	fuel	firing rate (Btu/h) ^a	flue gas parameters					ash inj temp (°C)	sampling duct parameters			
			flue gas at STP (m ³ /min)	% O ₂ (dry)	% CO ₂ (dry)	CO (ppm)	% H ₂ O		duct dia (cm)	av duct temp (°C)	sampling temp (°C)	res time ^b (s)
A	natural gas	40 000	0.38	9.5	5.4	12	9.9	450	14.3	285	257	2.91
B	natural gas	63 000	0.47	6.2	7.4	14	12.0	390	14.3	381	275	0.60
C	coal IBC109	40 000	0.36	9.3	8.7	100	4.5	450	14.3	315	268	2.89
D	coal Pitt no. 8	62 000	0.39	5.1	13.5	60	4.5	385	10.8	305	247	1.17

^a 1 Btu/h = 0.293 W. ^b Residence time in the horizontal duct only.

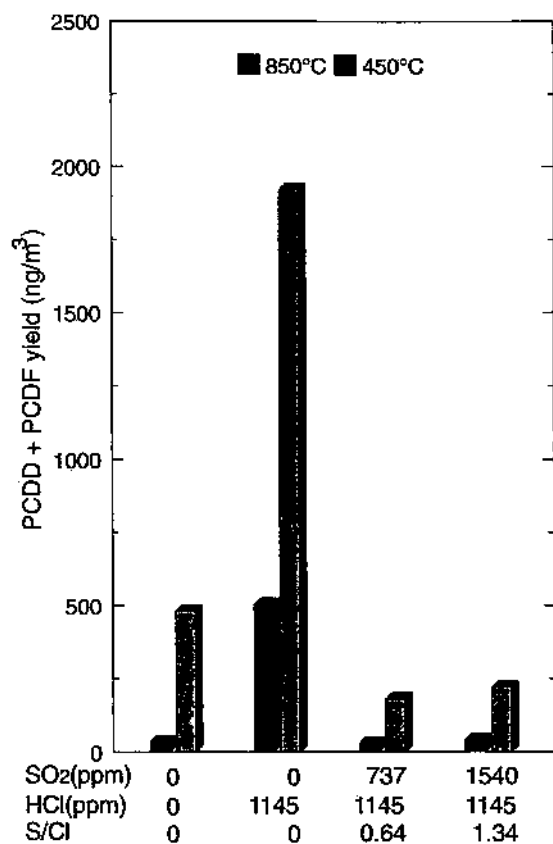


FIGURE 3. Total dioxin and furan yield in phase A IFR tests with MWC fly ash injection (natural gas).

Results and Discussion

Natural Gas-Fired IFR. Two series of tests were performed under natural gas-fired conditions. In each case, the furnace was doped with a constant level of HCl; SO₂ was injected at various rates to vary the S/Cl ratio. In phase A tests, the S/Cl ratio was varied at two MWC fly ash injection temperatures, 850 and 450 °C, and the results are shown in Figure 3 as total PCDD + PCDF yield. The SO₂ and HCl concentrations indicated are furnace concentrations, uncorrected for either H₂O or O₂, and the yields are nanograms of tetra-octa total per dry standard cubic meter of flue gas. The figures clearly show the inhibitory effect of S: in the presence of HCl, the yield is high when no SO₂ is added (S/Cl = 0) but decreases substantially for a S/Cl ratio of 0.64; further increase in the S/Cl made little difference to the reduced levels. The PCDD and PCDF tetra-octa congener distributions (not shown) reveal that, for our experimental conditions, a majority of these compounds are present as PCDF congeners. Reduction due to S is not congener-specific and appears to be distributed among all the congener classes. It is important to note that the S/Cl ratio at which the inhibitory S effect was observed in this work is the lowest reported in literature and much lower than the suggested value of 10 (2).

In addition to the S effects, the baseline test shown in Figure 3 indicates that, even with no added HCl, PCDD and PCDF yield is significant, especially at the lower MWC fly ash injection temperature. This implies that, since the PCDD and PCDF levels in the raw fly ash are relatively small (Table 2), the chlorine precursors on the MWC fly ash surface are in sufficient quantities to form PCDD and PCDF in the natural gas combustion environment. As expected, when HCl is added, the yield increases. These results also

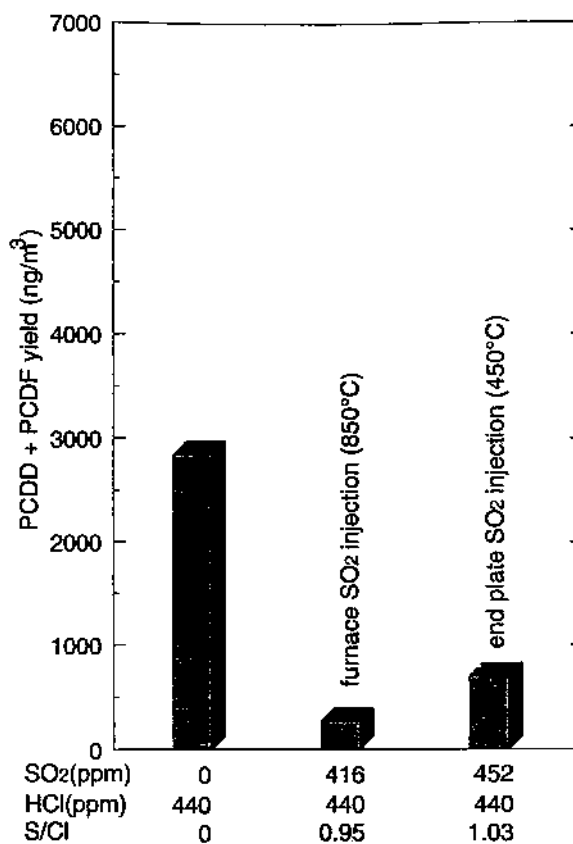


FIGURE 4. Total dioxin and furan yield in phase B IFR tests with MWC fly ash injection (natural gas).

support the previous finding that significant in-flight PCDD and PCDF formation takes place within the short residence times in the duct (17).

Considering the temperature effects, a higher MWC fly ash injection temperature results in lower PCDD and PCDF formation. This may be because in the presence of HCl the Cu catalyst on the MWC fly ash may form chlorides; the vapor pressure of copper chlorides is higher, and part of the Cu species in the fly ash might have vaporized at higher temperatures and recondensed downstream on the furnace walls, prior to reaching the PCDD and PCDF formation temperatures in the duct. This would result in fewer catalyst sites for PCDD and PCDF formation. The higher temperature may also deactivate the CuO catalytic sites due to sintering (18). It is also possible that higher temperatures may destroy organic precursors originally condensed on the as-received fly ash surface. However, the contribution of particle-bound organics toward PCDD and PCDF formation was found to be negligible compared to the effect of gas-phase organics resulting from natural gas combustion (19).

Phase B tests involve a different set of IFR conditions compared to phase A, particularly the firing rate, duct temperature, and residence time. The effect of S was verified at a S/Cl ratio of about 1, and the SO₂ injection temperature was varied. The PCDD and PCDF yields, shown in Figure 4, again demonstrate that the S inhibitory effect is substantial, irrespective of the SO₂ injection temperature. Thus, the mechanism of inhibition is not due to high-temperature gas-phase reactions between S species and organic precursors. Both phase A and phase B tests under natural gas-fired conditions demonstrate that inorganic S (as SO₂) is responsible for reducing the PCDD and PCDF formation.

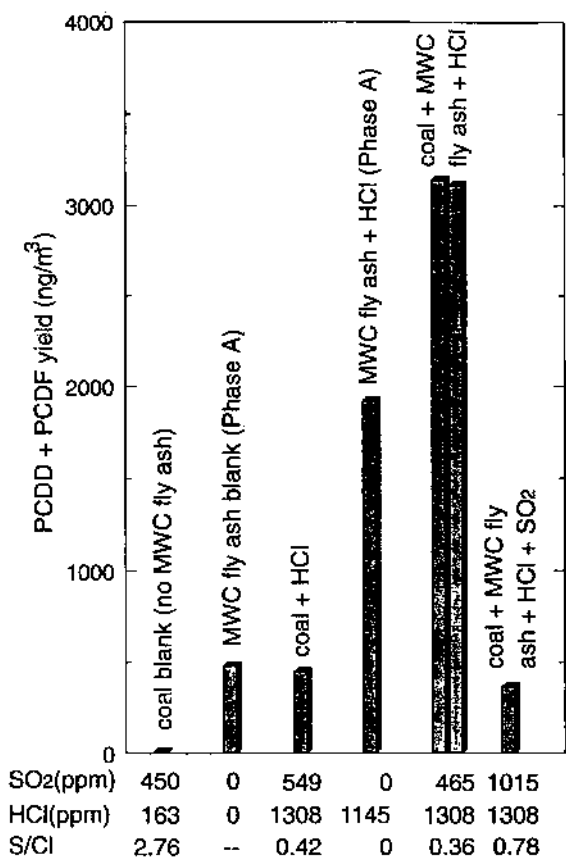


FIGURE 5. Total dioxin and furan yield in phase C IFR tests with MWC fly ash injection (IBC-109 coal).

Coal-Fired IFR. Results from the coal-fired IFR sampling are shown in Figure 5, and for comparison purposes, data from phase A natural gas tests are also included in the figure. The IBC-109 coal is a low-S, high-Cl coal; a coal blank test (without MWC fly ash) resulted in a HCl concentration of 163 ppm in the furnace. At this concentration, amounts of PCDD and PCDF formed were almost negligible. However, when the furnace was doped with HCl to a concentration of about 1308 ppm, some amounts of PCDD and PCDF were formed even without MWC fly ash. This implies that the coal combustion environment contains organic precursors that can form PCDD and PCDF.

When MWC fly ash was injected into the coal-fired furnace doped with HCl (coal + MWC fly ash + HCl), the PCDD and PCDF levels actually increased compared to the natural gas case (MWC fly ash + HCl) in spite of S present at a S/Cl ratio of about 0.4. Natural gas provides a cleaner burn than coal, and the higher concentration of organic precursors from coal combustion may offset the inhibitory effect of S. When the S/Cl ratio was further increased to 0.8 by doping additional SO₂ (coal + MWC fly ash + HCl + SO₂), the PCDD and PCDF yield dropped dramatically. As with natural gas tests, the PCDF congeners are in a majority, and the S inhibitory effect is distributed among all the congeners.

Phase D tests are with Pittsburgh no. 8 coal after substantial modifications to the IFR. Results are shown in Figure 6. Although there is no common set of conditions to compare directly with the results of previous phases, the PCDD and PCDF yields with the new IFR are substantially less, possibly due to better burn quality and/or lack of metal catalysts in the new refractory walls (19). However, the

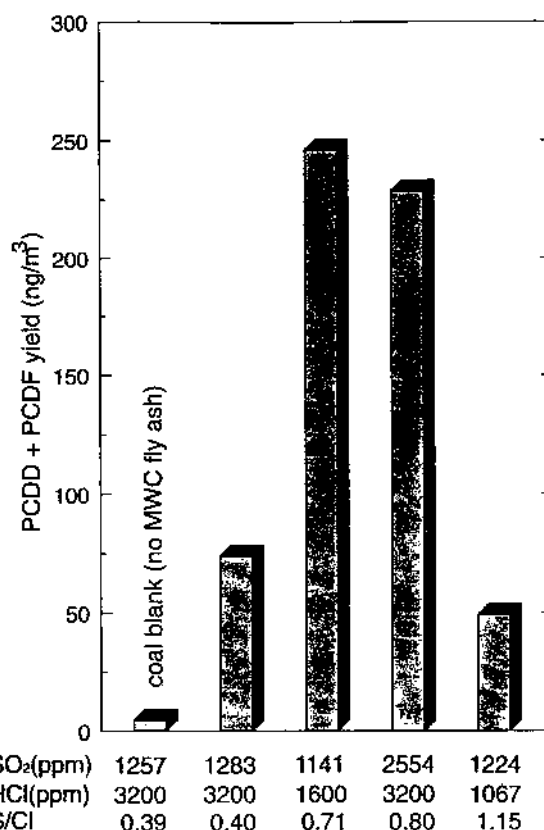
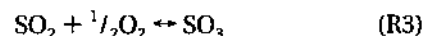


FIGURE 6. Total dioxin and furan yield in phase D IFR tests with MWC fly ash injection (Pittsburgh no. 8 coal).

results still indicate that at the higher S/Cl ratio (1.15) the PCDD and PCDF levels are much less.

These results clearly demonstrate the ability of S to inhibit PCDD and PCDF formation. Frankenhaeuser et al. (20) also observed a negative effect of SO₂ in the co-combustion of plastics with coal. Lindbauer et al. (14) added coal to a MSW incinerator and reported a dramatic decrease in yield with SO₂ levels at S/Cl ratios between 1 and 5. However, our work also shows that a coal combustion environment, especially when combined with MWC conditions, can in fact increase PCDD and PCDF yield if S/Cl ratio is not sufficiently high. Therefore, choice of coal type and MSW/coal firing ratio may be critical in achieving lower PCDD and PCDF levels through coal co-firing.

Inhibition Mechanism Studies. It has been shown that a chlorinating agent in PCDD and PCDF production is Cl₂, and HCl is relatively ineffective (4). Cl₂ is produced from HCl through the Deacon process (reaction R1), and the presence of SO₂ can convert the Cl₂ back to HCl through reaction R2. Equilibrium calculations were performed using NASA's CET89 computer code (21) for the HCl-SO₂-O₂-H₂O system to evaluate the possibility of Cl₂ depletion by SO₂. The results, however, showed that Cl₂ formation is always thermodynamically favored, the Cl₂/HCl ratio increases with decreasing temperature, and the results are virtually independent of SO₂ concentration. A closer analysis of the reaction equilibria shows that the combination of reactions R1 and R2 gives rise to



Thermodynamically, any set of two reactions among R1, R2, and R3 defines the system completely. For the typical initial concentrations used in the calculations (HCl and

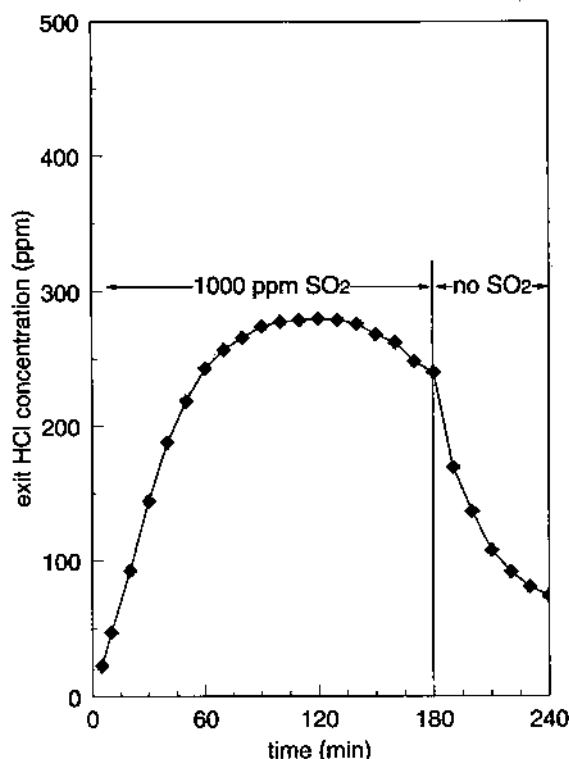


FIGURE 7. Gas-phase reaction between Cl_2 and SO_2 (400 °C, 500 ppm inlet Cl_2 , 10% O_2 , 3% H_2O).

SO_2 in ppm levels and O_2 and H_2O in percent levels), O_2 was in excess compared to HCl or SO_2 . Therefore, the equilibria for R1 and R3 are independent of each other; the equilibrium Cl_2 concentration depends only on R1 and that of SO_2 (or SO_3) depends only on R3, explaining the apparent lack of SO_2 effect on the Cl_2 concentration inferred from the thermodynamic equilibrium calculations for the HCl – SO_2 – O_2 – H_2O system.

The Deacon reaction (R1), although thermodynamically favored, is known to occur only in the presence of catalysts. In our bench-scale COR tests, a mixture of 1000 ppm HCl and 10% O_2 in N_2 was passed through the reactor at 400 °C, and the flow yielded a gas-phase residence time of about 10 s in the reactor. Observation of the HCl monitor at the reactor exit showed no decrease in HCl concentration, verifying that reaction R1 does not occur without the catalyst. Thus, Cl_2 production from HCl does not appear to be governed by the equilibrium thermodynamics of reaction R1, and information on reaction kinetics is needed for its determination.

Next, reaction R2 was considered separately, and equilibrium was calculated from the free energy and enthalpy data of the species involved (22). Results show that, over the entire temperature range, the Cl_2 – SO_2 reaction is strongly favored, and the amount of Cl_2 reacted was limited only by the available SO_2 . To verify this finding, the progress of reaction R2 was experimentally studied in the COR, under the scheme shown in Figure 2a. For the reactor temperature of 400 °C, the results are shown in Figure 7. The data clearly show HCl formation in the presence of SO_2 in accordance with reaction R2. This is consistent with the equilibrium calculation for reaction R2, although the maximum Cl_2 conversion or HCl concentration attained was less than the theoretical value of nearly 100% conversion. The data also show that, when SO_2 is replaced by N_2 , the HCl production drops sharply and approaches zero asymptoti-

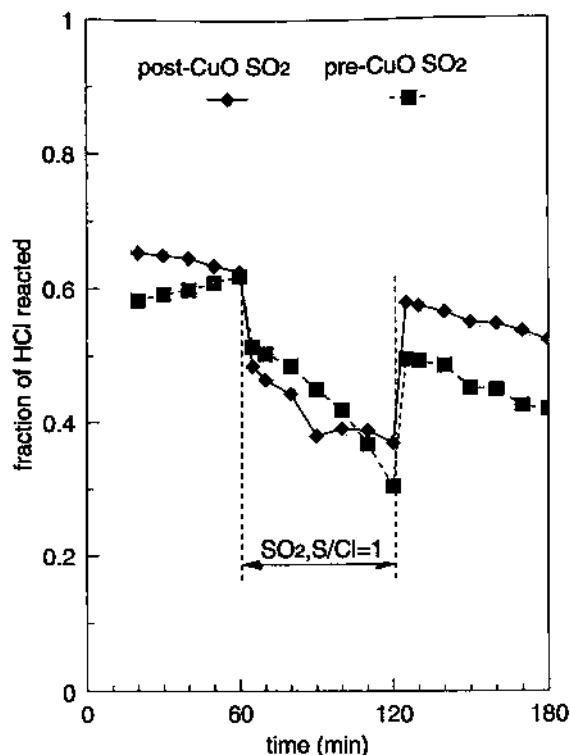


FIGURE 8. Comparison of SO_2 effects between gas-phase depletion and catalyst inhibition mechanisms toward chlorine production (1 g of CuO , 400 °C, 1000 ppm inlet HCl , 10% O_2).

cally, probably due to a large dead volume in the reactor. Nevertheless, the above discussions clearly demonstrate that the presence of SO_2 reduces available Cl_2 . Since gas-phase Cl_2 has been confirmed to be a major chlorinating agent in the PCDD and PCDF formation (4), Cl_2 depletion by SO_2 through homogeneous gas-phase reaction is a candidate mechanism for the inhibition of PCDD and PCDF formation by S.

Another mechanism of S inhibition has been shown to be the poisoning of Cu catalysts by SO_2 , which can inhibit (a) the biaryl synthesis of chlorinated precursors in the PCDD production and (b) the production of Cl_2 via the Deacon process in the temperature range 300–440 °C; the occurrence of the former was established (15). In this work, experiments were conducted to distinguish between the two possible S effects in reducing the Cl_2 availability—reduced Deacon process activity due to catalyst poisoning versus depletion of Cl_2 (produced from the Deacon process) through homogeneous gas-phase reaction (R2). The tests were conducted in the COR under the scheme shown in Figure 2b.

As described earlier under Experimental Procedures, tests were conducted in pairs and for 400 °C sample temperature. The results are shown in Figure 8. In both these tests, over the entire duration of the data, there is significant conversion of HCl , while in tests without the CuO sample, no HCl conversion was detected. Therefore, the conversion of HCl is due to CuO , suggesting Deacon process activity (reaction R1) and Cl_2 formation. The SO_2 effect is also noticeable in both the runs. The pre- CuO case represents SO_2 addition prior to the CuO sample, allowing for possible interference with the catalytic Cl_2 production as well as promoting the gas-phase reaction with the Cl_2 produced; the post- CuO case is when SO_2 was added immediately after the sample, which can only deplete

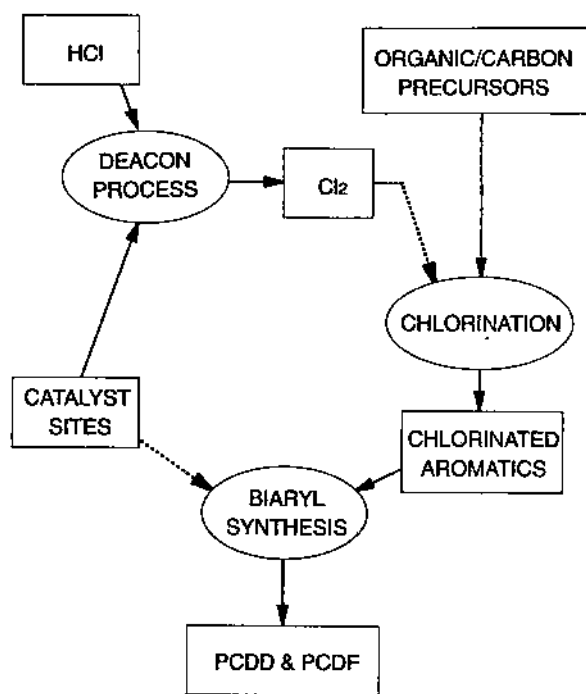


FIGURE 9. Overall reaction scheme for dioxin and furan formation at low temperatures (dotted lines are when S inhibition can occur).

the Cl_2 produced, without affecting the Deacon process activity. The shift in the overall HCl conversion profile with post-CuO SO_2 clearly demonstrates Cl_2 depletion due to the homogeneous gas-phase reaction (R2). The figure also shows that both pre- and post-CuO effects are nearly the same, suggesting that, for the studied experimental conditions, gas-phase reaction with Cl_2 is more dominant than catalyst poisoning. Although this comparison was made only at 400 °C, this is the temperature at which the CuO Deacon process activity is at its maximum, providing perhaps a greater potential for catalyst poisoning by S.

Thus, our results show that the depletion of available Cl_2 by SO_2 through homogeneous gas-phase reaction, noting that Cl_2 is the chlorinating agent, is a likely mechanism of S inhibition in PCDD and PCDF formation. Additional evidence comes from pilot-scale results shown in Figure 4, which show reduced PCDD and PCDF yield due to SO_2 injection. The S inhibition is more pronounced for furnace SO_2 injection compared to end plate injection. With the former, there is more time for SO_2 to react with Cl_2 , assuming that some Cl_2 is present upstream of the MWC fly ash injection location (end plate); although there is no added Cu source before the end plate, the reactor wall refractories may contain metal catalysts deposited from over 10 years of IFR operation (19).

A simple representation of the PCDD and PCDF formation steps at low temperatures is shown in Figure 9, assuming that the in-flight formation is through a surface condensation mechanism. Our results indicate that the SO_2 reduces the net Cl_2 production through gas-phase reaction rather than poisoning of the Deacon catalyst. The catalyst poisoning by S can still affect the PCDD and PCDF biaryl synthesis step significantly, which was also proven to be an inhibition mechanism by Gullett et al. (15). The steps where S inhibition can occur are represented in the figure by dotted lines. Based on the representation shown in the figure, in processes where the overall PCDD and PCDF yield is limited by the availability of either Cl_2 (not

HCl) and/or biaryl synthesis catalyst sites, the use of S can be effective in reducing PCDD and PCDF emissions. However, in MWCs, if S is introduced through coal co-firing, it is important to observe good combustion practices; otherwise increases in precursor concentration may offset the inhibitory effects of S. It is likely that, because of its Cl_2 depletion mechanism, S can also reduce the emissions of other chlorinated species such as polychlorinated biphenyls (PCBs) and polychlorinated phenols (PCPs).

This work does not address the possibility that the presence of S can affect PCDD and PCDF formation by sulfonating the phenolic precursors, preventing subsequent chlorination and biaryl synthesis, or by forming polychlorodibenzothiophene (PCDT) and polychlorothianthrene (PCTA), the S analogs of PCDD and PCDF (15).

Acknowledgments

The authors appreciate the logistical support of the late George R. Gillis (U.S. EPA/APPCD). Charles B. Courtney, Ann M. Drago, Ron Harrison, and Paul W. Groff (Acurex Environmental Corporation) and Jeff V. Ryan (U.S. EPA/APPCD) provided extensive sampling, technical, and analytical assistance. This work has been sponsored in part by the Illinois Department of Energy and Natural Resources (IDENR) through its Coal Development Board and Illinois Clean Coal Institute (ICCI). However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the view of IDENR and the ICCI.

Literature Cited

- (1) Stieglitz, L.; Vogg, H. On Formation Conditions of PCDD/PCDF in Fly Ash from Municipal Waste Incinerators. *Chemosphere* 1987, 16, 1917.
- (2) Griffin, R. D. A New Theory of Dioxin Formation in Municipal Solid Waste Combustion. *Chemosphere* 1986, 15, 1987.
- (3) Hagenmaier, H.; Kraft, M.; Brunner, H.; Haag, R. Catalytic Effects of Fly Ash from Waste Incineration Facilities on the Formation and Decomposition of Polychlorinated Dibenzop-dioxins and Polychlorinated Dibenzofurans. *Environ. Sci. Technol.* 1987, 21, 1080.
- (4) Gullett, B. K.; Bruce, K. R.; Beach, L. O. Formation of Chlorinated Organics During Solid Waste Combustion. *Waste Manage. Res.* 1990, 8, 203.
- (5) Gullett, B. K.; Bruce, K. R.; Beach, L. O. The Effect of Metal Catalysts on the Formation of Polychlorinated Dibenzop-dioxin and Polychlorinated Dibenzofuran Precursors. *Chemosphere* 1990, 20, 1945.
- (6) Ballschmiter, K.; Braunmiller, I.; Niemczyk, R.; Swerev, M. Reaction Pathways for the Formation of Polychlorodibenzodioxins (PCDD) and -furans (PCDF) in Combustion Processes. II. Chlorobenzenes and Chlorophenols and Precursors in the Formation of Polychlorodibenzodioxins and -dibenzofurans in Flame Chemistry. *Chemosphere* 1988, 17, 995.
- (7) Dickson, L. C.; Karasek, F. W. Mechanism of Formation of Polychlorinated Dibenzop-dioxins Produced on Municipal Incinerator Fly Ash from Reactions of Chlorinated Phenols. *J. Chromatogr.* 1987, 389, 127.
- (8) Karasek, F. W.; Dickson, L. C. Model Studies of Polychlorinated Dibenzop-dioxin Formation During Municipal Refuse Incineration. *Science* 1987, 237, 754.
- (9) Gullett, B. K.; Bruce, K. R.; Beach, L. O.; Drago, A. M. Mechanistic Steps in the Production of PCDD and PCDF during Waste Combustion. *Chemosphere* 1992, 25, 1387.
- (10) Stieglitz, L.; Zwick, G.; Beck, J.; Roth, W.; Vogg, H. On the de-novo Synthesis of PCDD/PCDF on Fly Ash of Municipal Waste Incinerators. *Chemosphere* 1989, 18, 1219.
- (11) Kimble, B. J.; Gross, M. L. Tetrachlorodibenzo-p-dioxin Quantitation in Stack-Collected Coal Fly Ash. *Science* 1980, 207, 59.
- (12) Ohlsson, O. O.; Livengood, C. D.; Daugherty, K. E. Results of Emissions and Ash Testing in Full-Scale Co-Combustion Tests of Binder-Enhanced dRDF Pellets and High-Sulfur Coal. Presented at Air and Waste Management Association Forum 90, Pittsburgh, PA, June 24-29, 1990.

- (13) Mahle, N. H.; Whiting, L. F. The Formation of Chlorodibenzo-*p*-Dioxins by Air Oxidation and Chlorination of Bituminous Coal. *Chemosphere* **1980**, *9*, 693.
- (14) Lindbauer, R. L.; Wurst, F.; Prey, T. Combustion Dioxin Suppression in Municipal Solid Waste Incineration with Sulfur Additives. *Chemosphere* **1992**, *25*, 1409.
- (15) 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*, 1938.
- (16) Environment Canada. Environmental Characterization of Mass Burning Incinerator Technology at Quebec City; Summary Report, National Incinerator Testing and Evaluation Program: Ottawa, June 1988; EPS 3/UP/5.
- (17) Gullett, B. K.; Lemieux, P. M.; Dunn, J. E. Role of Combustion and Sorbent Parameters in Prevention of Polychlorinated Dibenzo-*p*-dioxin and Polychlorinated Dibenzofuran Formation during Waste Combustion. *Environ. Sci. Technol.* **1994**, *28*, 107.
- (18) Satterfield, C. N. *Heterogenous Catalysis in Industrial Practice*, 2nd ed.; McGraw-Hill: New York, 1991.
- (19) Gullett, B. K.; Raghunathan, K. Observations on the Effect of Combustion Parameters on Dioxin/Furan Yield. Presented at Dioxin '95, 15th International Symposium on Chlorinated Dioxins and Related Compounds, Edmonton, Canada, Aug 21–25, 1995.
- (20) Frankenhaeuser, M.; Manninen, H.; Virkki, J.; Kojo, I.; Ruuskanen, J.; Vesterinen, R. The Effect of the Chlorine/Sulfur Ratio on Organic Emissions from the Combustion of Mixed Fuels. NESTE Final Report: Porvoo, Finland, 1992.
- (21) Gordon, S.; McBride, B. J. *Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations*; Scientific and Technical Information Office, NASA: Washington, DC, 1971.
- (22) Smith, J. M.; Van Ness, H. C. *Introduction to Chemical Engineering Thermodynamics*, 3rd ed.; McGraw-Hill: New York, 1975.

Received for review May 26, 1995. Revised manuscript received January 19, 1996. Accepted January 22, 1996.*

ES950362K

* Abstract published in *Advance ACS Abstracts*, March 15, 1996.