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Effects of gaseous NH_3 and SO_2 on the concentration profiles of PCDD/F in flyash under post-combustion zone conditions

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Abstract

The influence of gaseous ammonia and sulphur dioxide on the formation of 2378-substituted PCDD/F on a reference flyash from a municipal waste incinerator has been investigated using a laboratory scale fixed-bed reactor. The reference flyash samples (BCR-490) was reacted under a simulated flue gas stream at temperatures of 225 °C and 375 °C for 96 hours. The experiments were carried out in two series: first with simulated flue gas alone, and then with injection of NH_3 or SO_2 gas into the flue gas just before the reactor inlet. It was found that the injection of gaseous ammonia into the flue gas could decrease the concentration of both PCDD and PCDF by 34-75% from the solid phase and by 21-40% from the gas phase. Converting the results to I-TEQ values, it could reduce the total I-TEQ values of PCDD and PCDF in the sum of the flyash and exhaust flue gas by 42 - 75% and 24 - 57% respectively. The application of SO_2 led to 99% and 93% reductions in the PCDD and PCDF average congener concentrations, respectively in the solid phase. In the gas phase, the total reductions were 89% and 76% for PCDD and PCDF, respectively. Moreover, addition of SO_2 reduced the total I-TEQ value of PCDD and PCDF in the flyash and exhaust flue gas together by 60 - 86% and 72 - 82% respectively. Sulphur dioxide was more effective than ammonia in suppressing PCDD/F formation in flyash under the conditions investigated.

Keywords: Dioxins; PCDD/F; Incineration; Flyash

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1. Introduction

The emission of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) during combustion processes and in particular, the incineration of municipal solid wastes is still of serious concern to the public due to the adverse health effects of these toxic compounds. Particularly, the 2378-substituted PCDD/F congeners have been prominently portrayed as being highly toxic. De novo synthesis is a well researched formation route for PCDD/F in flyash within the post-combustion zone during combustion or incineration. Prevention of PCDD/F formation during the waste incineration process rather than removal of the already formed PCDD/F by end-of-pipe flue gas cleaning systems seems to be a promising technique. With the application of these techniques, the need is reduced for further treatment of the adsorbed or trapped PCDD/F on solid residues before disposal.

One of the encouraging techniques for in-process suppression of PCDD/F formation involves the use of chemical inhibitors. Over the last two decades several nitrogen compounds and/or in combination with sulphur compounds, have been examined as potential inhibitors for PCDD/F formation during waste incineration and other combustion processes. Among others, the PCDD/F suppressing effects of some solid inhibitors including urea, ethylenediammine tetraacetic acid (EDTA), monoethanolamine (MEA), and triethanol-amine (TEA), and some gaseous inhibitors such as ammonia (NH_3), sulphur dioxide, amido sulphonic acid and dimethylamine (DMA) have been reported (Addink et al., 1996; Ruokojarvi et al., 1998; Tuppurainen et al., 1999; Samaras et al., 2000a; Samaras et al., 2000b; Ruokojarvi et al., 2001; Xhrouet et al., 2002; Kuzuhara et al., 2005; Marie-Rose et al., 2009; Williams, 2005).

In literature, various mechanisms have been proposed for the suppression of PCDD/F formation in the presence of nitrogen- and sulphur containing compounds.

Most of the mechanisms involve reducing the ability of metals to catalyse PCDD/F formation. The proposed mechanisms of PCDD/F inhibition by nitrogen compounds include alteration of acidity of flyash e.g. by ammonia; formation of stable metal nitride bonds; and formation of stable metal-ammonia co-ordination compounds (Ismo et al., 1997, Tuppurainen et al., 1998; Kuzuhara et al., 2005). However, some mechanisms also involve the reaction of the nitrogen-based additives and their degradation products with PCDD/F precursors. For example, during combustion NH_i and CN radicals may form and can become attached to potential aromatic rings or may even be inserted into the rings forming aromatic amines, nitriles and pyridine-like structures (Kasai et al., 2008). Recently, Marie-Rose et al. (2009) proposed that PCDD/F could be removed from flue gas via oxidation by NO_2, produced from the prior oxidation of the ammonia additive.

The main suggested mechanisms involved in the suppression of PCDD/F by sulphur-containing compounds can be summarized as follows: i) Homogenous reduction of Cl_2 at high temperature to HCl which is less active than Cl_2 in the chlorination reactions. ii) Conversion of metal oxide/chloride catalyst to metal sulphates which show less catalytic activity, therefore reducing the catalytic activity of the ‘Deacon Reaction’. and iii) SO_2 sulphonates the phenolic precursors which prevents chlorination and bi-aryl synthesis, and promotes the formation of sulphur analogues of PCDD/F (Ogawa et al., 1996, Tuppurainen et al., 1998; Ryan et al., 2006; Ke at al., 2010). In addition, Addink et al. (1996) showed that sulphur-based inhibitors were capable of changing the number of chlorine atoms built into PCDD/F molecules but not the position of chlorination.

The variation of mechanisms as well as the inhibitory effects of additives on PCDD/F formation could be due to a number of factors. These could include the type and configuration of plant (Addink et al., 1996), the concentration and form of application of the particular additive (Furrer et al., 1998; Bechtler et al., 1998; Ruokojarvi et al., 2004; Kuzuhara et al., 2005), the point of application within the plant (Kasai et al., 2008), the operating temperature of the plant (Jansson, 2008; Weber et al., 1999; 2002; Lundin, 2007; Cunliffe and Williams, 2007) as well as composition of the fuels.

It would appear that the catalytic activity of metals during de novo synthesis of PCDD/F would involve both solid-solid as well as gas-solid interactions on the flyash. However, operating temperature has consistently appeared to be an important factor affecting the formation of PCDD/F in flyash (Weber et al., 1999; 2002; Lundin, 2007; Cunliffe and Williams, 2007; Jansson, 2008). Hence, temperature may also influence the ability of additives in suppressing PCDD/F formation. For example, Ruokojarvi et al., (1998) separately examined the inhibitory effects of gaseous compounds such as SO_2 and NH_3 on PCDD/Fs formation. The additives were sprayed directly into the flue gas stream at the temperatures of 670 °C and 410 °C respectively. The total PCDD/Fs concentration was reduced by 42 - 78% with the large amount being reduced in particulate phase. Similarly, Ruokojarvi et al., (2004) reported that spraying gaseous ammonia into the flue gas during the combustion of light heating oils in a pilot-scale incinerator could reduce the PCDD/F concentration in the flue gas by 68% at 410 ºC. In the same vein, Addink et al., (1996) reported that the addition of sodium sulphide reduced PCDD/F concentration on flyash by 80 – 90% during the thermal treatment of flyash in a fixed-bed reactor at around 300 ºC.

In most cases, studies showed that PCDD/F congeners were subjected to desorption/volatilization and degradation/dechlorination at temperatures of about 500 °C (Weber et al., 1999; Cunliffe and Williams, 2007). On the contrary, lower temperatures have been found to favour de novo formation of PCDD/F (Lundin et al., 2007; Jansson, 2008; Lundin et al., 2011). The combination of these reactions could lead to shifts in the degree of chlorination of the PCDD/F in relation to temperature. A plausible consequence of such changes in the degree of chlorination may involve increases in the concentrations of the most toxic 2378-substituted congeners. For example, Cunliffe and Williams (2007) reported that treatment of incinerator flyash under inert (nitrogen) gas at 375 ºC for 4 d resulted in almost 200 times increase in the concentration of the highly toxic 2378-TCDD compared to the unreacted flyash sample.

This paper describes the changes in the concentration profiles of the toxic 2378-substituted PCDD/F congeners in a reference flyash sample in relation to temperature under simulated flue gas conditions. The selected temperatures of 225 ºC and 375 °C are respectively, within the window for dioxin formation via de novo synthesis. Experiments have been carried out with a laboratory scale static-bed reactor. Most importantly, the effects of the injection of gaseous ammonia and sulphur dioxide into the flue gas, on the concentrations of the PCDD/F congeners have been studied under these conditions. In addition, changes in the total toxic equivalency of PCDD/F in the treated samples are reported.

2. Materials and methods

2.1. Experimental procedures

A laboratory scale fixed-bed reactor was developed and used to investigate the influence of gaseous ammonia and sulphur dioxide on PCDD/F formation on MWI flyash at the temperature windows of the post combustion zone. It has been accepted that the most effective temperature zone for PCDD/F formation via de-novo synthesis is between 200 and 400 ºC (McKay, 2002; Stanmore, 2004). Hence, experiments were carried out at temperatures of 225 and 375 ºC, respectively. A schematic diagram of the experimental reactor is shown in Figure 1. The reactor consisted of a tubular stainless steel reactor with a removable quartz lining surrounded by a temperature-controlled cylindrical furnace. The reactor was of 25 cm height, 48 mm inner diameter with a purge gas inlet at the top, and equipped with a thermocouple to detect the sample bed temperature. BCR-490 reference flyash sample was used for this study.

The metal contents of the applied reference flyash were analyzed via acid digestion and flame atomic absorption spectrometry methods before the experiments. The major metals found were iron (12.3 mg/g), magnesium (9.13 mg/g)) and lead (7.50mg/g). In addition, small amounts of copper (0.68 mg/g) was found which could be a source of metal catalyst for promotion of PCDD/F formation on the flyash (Hinton and Lane, 1991). A 25 wt% flyash sample in sand was prepared by mixing 2 g of BCR-490 certified reference material with 6 g pre-cleaned analytical sand, in order to increase the porosity and gas-particle contact surfaces. The mixture was placed on the sample boat composed of glass fibre filter supported with a sintered glass frit inside the quartz lining and treated at the individual temperatures under a constant flow of 120 ml min^{-1} simulated flue gas for 96 h.

The experiments were carried out under the same operational conditions in two series; first with simulated flue gas alone, and second with the injection of either gaseous NH_3 or sulphur dioxide just before the reactor inlet. The simulated gas mixture contained 4.8 vol.% O_2, 9.6 vol.% CO_2 and 20.0 vol.% H_2O in N_2. The nominal concentrations of NH_3 and SO_2 in gas mixture were 1000 ppm and 2000 ppm, respectively. These levels of NH_3 and SO_2 were chosen in relation to the previously applied ranges in the literature (Johnke and Stelzner, 1992; Raghunathan and Gullett, 1996). It is generally assumed that the SO_2 concentration in the real world flue gas could be between 500-2000 ppm and that of for NH_3 might vary between 100-1000 ppm (Kuzuhara et al., 2005). The H_2O was supplied by peristaltic pump micro-injector. The water was converted to steam by passing through a small stainless steel tube located inside the furnace and then injected into the reactor at the same temperature to prevent condensation. The flow rate of water injected was adjusted to 1ml h^{-1} by calculation to achieve a water vapour concentration of 20% in the flue gas mixture.

The 2378-substituted PCDD/F congeners released to the exhaust gas from the reactor were collected by a tertiary trapping system. The first trap was an empty dreschel bottle located in an ice/water bath to act as a water vapour condensation system, connected directly to the reactor outlet tube. The second trap was a glass tube containing pre-cleaned Supelco amberlite polymeric XAD-II resin, held in place with pre-cleaned Orbo polyurethane foam (PUF) plug. The resin was cleaned by solvent extraction and spiked with $^{13}C_{12}$-labelled 2378-substituted PCDD/F standards prior to application. An empty dreschel bottle was used as a third trap to completely condense the exhaust gas and to capture any escaping species. Silicon tube was utilized for tubing of the trapping system. The resin trap was covered with aluminum foil to prevent UV degradation of the dioxins.

2.2. Chemical standards and organic solvents

A set of five calibration standard solutions (CS1-CS5) containing the 17 toxic congeners of native PCDD/F (2,3,7,8-positional substitutes) at concentrations between 0.5 and 2000 ng ml^{-1} and corresponding $^{13}C_{12}$ isotope enriched PCDD/F at 100 ng ml^{-1} (except for $^{13}C_{12}$ -OCDD which was 200 ng ml^{-1}) with a purity of ≥ 99% were used. The $^{13}C_{12}$ labelled standard stock solution containing 17 toxic congeners of PCDD/F at the concentration level of 100 ng ml^{-1} (except for $^{13}C_{12}$ -OCDD which was 200 ng ml^{-1}) were used to quantify the corresponding native compounds by the isotope dilution method. This solution was added to the samples just before the extraction process. However the XAD-II resin which was applied for dioxins trapping from the exhaust gas of the reactor was spiked just before application throughout the experiments. Furthermore an internal standard solution containing isotopically labelled $^{13}C_{12}$-1234-TCDD and $^{13}C_{12}$-123789-HxCDD at a concentration level of 200 ng ml^{-1} in nonane were added to the purified extract prior to GC injection as syringe standards for the determination of recovery percentages of labelled dioxins. All these standards were purchased from LGC Standards, UK; (supplied by CIL Inc. MA, USA). The gaseous ammonia, SO_2 gas and simulated gas mixtures were supplied by BOC Special Gas, Ltd. UK. All the organic solvents such as acetone, toluene, dichloromethane, n-hexane, ethyl acetate, used for extraction, clean-up and glassware rinsing, were certified grade for the dioxins analysis and purchased from Sigma-Aldrich, Ltd. UK.

2.3. PCDD/F extraction, clean-up and Analysis

The US-EPA method 1613 was applied for the analysis of PCDD/F in solid matrices (US-EPA, 1994). The reacted flyash samples collected from the reactor after the experiment were primarily digested with HCl 10 M, filtered, rinsed with distilled water and dried in an oven at 105 ºC for 1 h. In all the experiments, the filter containing the reacted flyash sample was taken out and consequently extracted along with sample, thus preventing any sample losses during sampling and analysis. The samples were then spiked with $^{13}C_{12}$-labelled PCDD/F toxic congeners prior to extraction and left to equilibrate for 2 h by occasionally tumbling the samples. The samples were loaded into the 11 ml extraction cell and extracted using a Dionex ASE-100 solvent extraction unit with toluene as an extraction solvent. Based on EPA method 3545A, the extraction method of the ASE system was set for a temperature of 200 ºC and pressure of 1500 psi (Richter et al., 1997, Dionex, 2005). The XAD-II resin with PUF plugs were extracted with a 50/50 mixture of acetone and hexane using the ASE at 100 ºC and 1500 psi.

The condensate in the first trap was liquid extracted three times with 15 ml toluene and the extracts with the trapping line washes were added to the main XAD-II resin extract, all together representing the sample for gas phase PCDD/F analysis. The procedure for sample preparation including the concentrations steps, clean-up using the automated Power-Prep^{TM} Fluid Management System (FMS) and micro-concentration have been described in detail in an earlier paper (Hazejadeh et al., 2011). The glassware, dreschel bottles and reactor lining were washed with detergent, rinsed out with toluene, hexane and acetone subsequently, and cleaned in an ultrasonic batch before use. All the experiments were performed in duplicate and the average of the results was considered along with the standard deviations. A final sample volume of 10 µL in nonane was achieved prior to analysis.

The analyses of the 2378-substituted PCDD/F were performed using a gas chromatograph attached to a triple quadrupole mass spectrometry system (GC-MS/MS QqQ). A Varian 450-GC coupled with a Varian 320-TQ-MS equipped with a Varian 8400 auto-sampler was applied. The GC separation of PCDD/F was carried out using a Varian CP-Sil 88 capillary column for dioxins (50 m × 0.25 mm I.D, 0.25 µm film thickness). The column oven temperature program was initially 140 ^{0}C held for 2 min., ramp at 45 ^{0}C min^{-1} to 190 ^{0}C with no holding time, and ramp at 5 ^{0}C min^{-1} to 240 ^{0}C held for 31.89 min. gaining the total runtime of 45 min. This method enables the rapid elution of the solvent in injected sample matrices and best separation of PCDD/F throughout the column. Helium was used as a carrier gas at a constant flow-rate of 1ml min^{-1}. Samples were injected to the GC in split/splitless injection mode with the amount of 2 µl and the injector temperature was kept at 270 ^{0}C. The retention time was categorized to 11 segments and the corresponding scan method for each segment was introduced in order to avoid the co-elution of PCDD/F isomers (Cunliffe and Williams, 2006; Hazejadeh et al., 2011). Quantification of PCDD/F was carried out according to US-EPA method 1613 procedures using internal standard and isotope dilution methods (US-EPA, 1994). Relative response (RR) and response factor (RF) for each individual compounds were calculated with the corresponding calibration standard solutions (Hazejadeh et al., 2011).

3. Results and Discussion

Table 1 shows the results obtained from the analysis of toxic PCDD/F in the reference flyash samples, including the certified values and the concentrations of these congeners in relation to temperatures after thermal treatment for 96 h. Although, no certified values were reported for two PCDD and three PCDF congeners, the analytical results obtained from the unreacted reference sample, suggest that the procedures used in this work were fit-for purpose and gave reliable results. For instance, the mean coefficient of variation between the certified values and this work was 1.96% for the PCDD and 5.58% for the PCDF congeners, respectively, which was calculated using their concentrations in ng/kg. Also, the slight discrepancy in the PCDD/PCDF I-TEQ ratios between the certified values (0.89) and the analytical results from this work (0.83) is acceptable in dioxin analyses (US-EPA, 1994; European commission, 2007). In general, the average results of duplicate experiments were presented with percentage standard errors which varied from 0.18% to about 16%.

3.1. Effect of temperature on PCDD/F homologue patterns

As shown on Table 1, temperature has an immense effect on the formation of the PCDD/F congeners in the flyash. Literature shows that both formation and degradation of PCDD/F could occur during these reactions (Cunliffe and Williams, 2007; Jansson et al., 2008); however these results show that the rate of formation of the PCDD/F was most certainly higher than the rate of destruction at the tested temperatures. Dramatic increases in the concentrations of the toxic PCDD/F were observed at both 225 °C and 375 °C compared to unreacted flyash sample for all the congeners examined.

Interestingly, the concentration of 2378-TCDD increased by about 32 times at 225 °C but the increase was only about 11 times at 375 °C. Similar reduction in concentrations was observed for the highly chlorinated PCDD congeners including 123789-HxCDD, 1234678-HpCDD and OCDD. A closer scrutiny would reveal that the concentrations of 1234678-HpCDD and OCDD were nearly halved at 375 °C compared to 225 °C. In contrast, the concentrations of 12378-PeCDD, 123478-HxCDD and 123678-HxCDD increased with temperature. For instance, the concentration of 12378-PeCDD nearly doubled, while that of 123478-HxCDD increased about four times at 375 °C compared to the lower temperature. This may be due to dechlorination and/or degradation of the highly chlorinated congeners. Generally, the total concentration of the PCDD was about 79900ng kg^{-1} at 225 °C but this decreased by 9.0% to 72700 ng kg^{-1} at 375 °C. In terms of toxicity equivalency, the total ITEQ for the PCDD was 14600 ng ITEQ kg^{-1} at 225 ºC, but increased slightly by 11% to 16400 ng I-TEQ kg^{-1} at 375 ºC.

In most cases, dramatic increases in the concentrations of the 2378-substituted PCDF congeners were observed at 375 ºC compared to 225 ºC. For example, compared to its level in the unreacted flyash, the concentration of 2378-TCDF increased 58 times at 375 ºC but it was just 6 times at 225 ºC. Generally, the concentrations of most of the

PCDF congeners were about 4 times higher at 375 ºC than at 225 ºC. However, the concentrations of 23478-PeCDF, 1234789-HpCDF and OCDF remained largely unchanged after 96 h reaction at both temperatures. In total, 90500 ng kg^{-1} of 2378-PCDF was formed at 225 ºC compared to 212500 ng kg^{-1} at 375 ºC. In terms of toxicity equivalency, the total PCDF formed at 375 ºC was 42% more toxic than those formed at 225 ºC.

Comparing the separate data for the PCDD and PCDF congeners, it can be seen that higher formation of the PCDF were obtained. This is in agreement with literature, which shows that PCDF are more preferentially formed via de novo synthesis than the PCDD homologues (McKay, 2002; Stanmore, 2004). While the PCDD showed evidence of dechlorination or degradation of the highly chlorinated homologues, the same was not obvious with the PCDF congeners. Apart from the 2378-substituted congeners, other PCDD/F compounds would be present in the flyash. The degradation and isomerization of these other congeners may have affected the concentrations of the toxic congeners measured in this work.

Fig. 2 shows the distribution of the 2378-subsitututed PCDD/F at 225 ºC [a] and 375 ºC [b], respectively in both the gas and solid phases after 96 h reaction time. At 225 ºC, apart from 23478-PeCDF, higher concentrations of the other congeners were found in the solid phase than in the gas phase, indicating that the rate of formation and retention of the congeners on the solid matrix was higher that their rate of desorption into the gas phase. However, exactly the opposite phenomenon was observed at 375 ºC, where majority of the PCDD/F concentration was in the gas phase. This was not surprising as according to Cunliffe and Williams (2007), desorption of PCDD/F into the gas phase should increase with temperature, reaching a maximum around 350 °C. It is also clear from the Fig. 2 (a and b), that the sum of the concentrations of the PCDD/F congeners at 375 ºC was more than twice their total concentration at 225 ºC, which suggest active formation of the congeners within the temperature range studied in this work.

3.2. Effect of gaseous ammonia on PCDD/F homologue pattern

The sum of the concentrations of 2378-substituted PCDD/F in both the gas and solid phases after the reactions with adding NH_3 are also presented in Table 1. No significant changes in the homologue patterns by NH_3 addition were observed compared to the experiments without NH_3 at the tested temperatures. It suggests that varying the temperature within the tested range did not significantly affect the mechanism of PCDD/F inhibition by ammonia. This was consistent with the results reported by Ruokojarvi et al., (1998).

In general, a clear decrease in the concentrations of both PCDD and PCDF congeners occurred when NH_3 was injected into the reactor. Studying the effects of nitrogen compounds on PCDD/F formation, Addink et al. (1996) reported that addition of 2-10% nitrilo-triacetic acid (NTA) into an organic-free MWI flyash in the presence of HCl as a chlorinating agent reduced both the PCDD and PCDF by more than 50%. However similar to our results no changes in isomer distribution was observed (Addink et al., 1996) .

Detailed effects of NH_3 injection on PCDD/F concentrations in the solid and gas phase are presented in Table 3. The percentage reductions were calculated based on the concentrations of PCDD/F congeners in experiments without any additives. Interestingly, all the PCDD congeners showed reductions in the presence of gaseous ammonia, however the reductions on the lower chlorinated isomers from the solid phase was greater than the highly chlorinated ones at the examined temperatures. For example, 2378-TCDD and 12378-PeCDD reduced by 91% and 71% respectively, whereas 1234678-HpCDD and OCDD reduced by 8.6% and 12%, respectively. In general, the average reduction in the concentrations of the PCDD with the application of ammonia was about 51% at 225 ºC. This value comprised of a 49.9% reduction in the solid phase and 51.5% reduction in the gas phase at this temperature. At 375 ºC, an average reduction of PCDD concentrations of 64.2% was achieved. Also, the reduction at 375 ºC comprised of 71.7% on the solid phase and 56.7% on the gas phase.

The result for the PCDF congeners was very different without any clear trends in the reduction of their concentrations in the presence of ammonia. On the average, slightly more reduction was observed in the solid phase compared to the gas phase at 225 ºC. However, at 375 ºC, the average reduction on the solid phase PCDF was nearly ten times the reduction on the gas phase. In fact, only 3.96% reduction was achieved in the gas phase compared to 36% in the solid phase at 375 ºC. In Table 3, the negative reduction values for most PCDF actually imply a net formation of these toxic compounds even in the presence of ammonia. For instance, a net 40% increase in the concentration of the most toxic 2378-TCDF was observed in the solid phase at 375 ºC. However, about 60% reduction in the gas phase was achieved at the same temperature. Hence, an average reduction of 12% was achieved for 2378-TCDF at 375 ºC, which was similar to the 10.5% average reduction for the congener at 225 ºC. In contrast, OCDF gave a net average formation of 28% at 225 ºC, and 12% at 375 ºC. In addition, 1234789-HpCDF and 12378-PeCDF showed net average formations at 375 ºC, especially from the gas phase. Percentage reduction was highest for 123789-HxCDF of all the congeners at both 225 ºC and 375 ºC, respectively. Compared to the work without ammonia, it can be seen that this congener, along with 2378-TCDF, 1234789-HpCDF and OCDF, has the lowest concentration in the fresh reference flyash. In addition, their concentrations, in terms of balance of formation and destruction without ammonia, were also among the lowest. However, it is not clear why both 2378-TCDF and 123789-HxCDF gave the highest reduction and why 1234789-HpCDF and OCDF gave the highest formation in the presence of ammonia under these test conditions. These results are comparable with the results reported by Ruokojarvi et al. (1998), who found that there was more reduction in the particulate phase than that in the gas phase when the gaseous ammonia was injected between two economisers at a temperature range of 670 to 410 ºC. They reported that the total PCDD/F concentration was reduced by between 42% and 78%.

Figure 3 shows the sum of the solid and gas phase reductions of PCDD/F toxic equivalency values by using NH_3 in relation to different reaction temperatures. Application of ammonia could decrease the total I-TEQ value of PCDD and PCDF in flyash and exhaust flue gas together by 42% to 75% and 24% to 57% respectively at different reaction temperatures. The total highest reduction of 57% in PCDD/F I-TEQ value was achieved at 225 ºC. The results indicated that the reduction of the low substituted congeners with high toxic equivalency value at 225 ºC was more favourable than at the higher temperature of 375 ºC.

Results from this work showed that the inhibitory effect of gaseous ammonia on PCDD/F formation vary largely among the congeners studied. Through the 96 h of reaction (4 days) in this work, there was strong evidence of the suppression of PCDD/F formation even under conditions suitable for their active de novo synthesis. This makes gaseous ammonia potentially suitable for use in the post-combustion zone of an incinerator. Separate analysis of solid-phase and gas-phase PCDD/F concentrations showed that ammonia may have affected the solid phase interactions involving the catalytic metals present in the flyash.

3.3. Effect of SO_2 on PCDD/F concentration profiles

The sum of the concentrations of 17 toxic PCDD/F congeners in both solid and gas phases, with SO_2 injection into the reactor are presented in Table 1 in relation to temperature. Compared to the work without SO_2, considerable decrease in both PCDD and PCDF concentrations were observed particularly at 375 ºC. These results are consistent with the results of Ke et al., (2010), who reported a remarkable decrease in PCDD/F formation during the treatment of a model flyash samples at 300 ºC under simulated flue gas containing 150 ppm SO_2. No obvious differences in the behaviour of individual congeners in relation to SO_2 addition were observed at the tested temperatures. This also agrees with the work of Shao et al., (2010) who found that the addition of SO_2 into the inlet gas of a model ash treatment process at 350 ºC with a S/Cl ratio of 0.25, could reduce the PCDD/F levels by about 90%. However, there was no noticeable influence on PCDD/F homologue distribution and isomer profiles (Shao et al., 2010). In this work, reduction in the formation of most toxic furan, 2378-PCDF, appeared to be higher than other congeners. Generally, at 225 ºC the reduction of PCDD congeners was higher than PCDF, but in the experiments at 375 ºC the PCDF were reduced more than PCDD. This is in agreement with the results of a similar study conducted by Chang et al., (2006), who added elemental sulphur into the flyash of a municipal waste incinerator which was reacted at 300 ºC under a gas stream. The sulphur in flyash reduced the PCDD/F formation by 72% in terms of I-TEQ values.

The [PCDF]:[PCDD] ratio of the resultant PCDD/F concentrations was 1.1 without SO_2 at 225 ºC, but this ratio fell to 0.6 on addition of SO_2. At 375 ºC, the ratio was 2.9 without SO_2 but increased to 6.1 in its presence. These results were similar to those obtained when ammonia was used, indicating that significantly higher PCDF were formed at higher temperatures in the presence of these additives than the PCDD congeners. The reverse was the case at lower temperatures, where the formation of PCDD was predominant. This indicates that the inhibition mechanisms may be highly temperature dependent and likely different for PCDD and PCDF, respectively. It has been reported that the suppression effects of sulphur-containing compounds are higher for lower chlorinated PCDD and higher chlorinated PCDF (Pandelova et al., 2005; 2007). In addition, Chang et al. (2006) reported that PCDD/F inhibition in the particulate-phase was more than the gaseous-phase and PCDD was reduced more than PCDF. However, in contrast to the results from this work, Aurell et al. (2009) reported recently that the inhibitive effect of SO_2 on PCDF formation was more than that on PCDD formation. These discrepancies in results suggest that the effects of an inhibitor may be different depending on the point and concentration of injection of the SO_2 and the temperature of the flyash bed. Varying in the SO_2 concentration would affect the SO_2:HCl or S:Cl mass ratios, which could significantly influence the PCDD/F formation and their isomer patterns in the flue gas (Aurell et al., 2009).

Detailed data on the percentage reduction of individual PCDD/F in the solid and gas phases at the two temperatures are presented in Table 4. Among the PCDD congeners, in experiments at 225 ºC the concentration of low chlorinated congeners in the solid phase considerably decreased in the presence of SO_2. For instance, 94% reduction was achieved for 2378-TCDD. In contrast, SO_2 injection appeared to slightly increase the concentrations of some highly chlorinated congeners at this temperature. Hence the average reduction of PCDD congeners in the solid phase was 30% at 225 ºC. However, net formation of PCDD congeners was observed in the gas phase compared with experiments without SO_2. Table 4 shows negative values for the percentage reductions of the PCDD congeners in the gas phase, indicating an average formation rate of 55% at this temperature. It could be the case that SO_2 promoted desorption of the remaining PCDD congeners from the reacted flyash into the gas phase, so that increasing the gas/solid ratio of PCDD (Ke et al., 2010).

On the contrary, all the PCDF congeners except OCDF showed marked reduction by the application of SO_2 at 225 ºC. OCDF gave a net formation percentage of 28% but the average of 50% reduction was achieved for all the PCDF congeners in the solid phase. However, a reverse trend was observed in the gas phase, where net formation was observed for all but two of the PCDF congeners, namely 2378-TCDF and 23478-PeCDF. In fact, on average a net formation rate of 38% was observed for gas-phase PCDF at 225 ºC.

Interestingly, no net formation of any of the PCDD/F congeners was observed at 375 ºC. Substantial reductions in the PCDD concentrations were achieved with values of between 91 and 100 % (99% average) in the solid phase on application of SO_2. Also very high reduction percentages were achieved in the gas phase, with an average of 89% for all the PCDD. Although, the percentage reduction of PCDD was higher than the PCDF, the overall reduction was very significant in the latter. In the solid phase, the average reduction for the PCDF congeners was 93%, while it was 76% in the gas phase. This suggests that temperature has a profound effect on the ability of SO_2 to act as an inhibitor for PCDD/F formation in flyash. These results are in agreement with some previously reported results using sulphur compounds as inhibitors. For example, during the combustion of chlorinated waste in a bench-scale quartz liner reactor at 320 ºC (Lee et al., 1998) the injection of gaseous SO_2 into the flame zone of the reactor resulted in a lower PCDD/F emission. Furthermore, similar to the results here, sulphur was more effective for the inhibition of PCDF formation than PCDD formation (Chang et al., 2006).

Consistent with a previous report by Ruokojarvi et al. (1998), reduction of PCDF in the solid phase was slightly higher than that in the gas phase. This could be partly attributed to the suggestion that SO_2 can increase the gas/solid ratios of PCDD/F via promoting desorption of PCDD/F from the flyash matrix (Ke et al., 2010).

Figure 3 demonstrates the sum of the solid and gas phase reductions of the PCDD/F toxic equivalency values by SO_2 in relation to the two temperatures studied in this work. Addition of SO_2 into the reactor inlet reduced the total I-TEQ value of PCDD and PCDF in the flyash and exhaust flue gas together by 60 - 86% and 72 - 82%, respectively. The total reduction in the PCDD I-TEQ value was a minimum 58% at 225ºC and reached 84% at 375 ºC. Also, for the PCDF congener, the total reduction in I-TEQ was 70% at 225 ºC and nearly 75% at 375 ºC. These reduction efficiencies are high compared to the results of a previous study conducted by Pekarek et al. (2007), who reacted a homogenized mixture of dioxin-free flyash, NaCl, $CuCl.2H_2O$, and carbon at 340 ºC under a flow of SO_2 in O_2/N_2. The difference between the reductions obtained by Pekarek et al. and this work could be attributed to the differences in the concentration of SO_2, the reaction time, and the composition of the simulated flue gas composition between the two sets of experiments. While these authors did not provide data on the concentration of SO_2 used, the differences in reaction time and flue gas composition could significantly affect the two results. These authors obtained decreases in the toxic equivalency values by 35% for PCDD and by 20% for PCDF, which showed that the inhibitory effect of SO_2 was significantly more pronounced for PCDD than that for PCDF, similar to our results. The results of the present study reveal that application of SO_2 as an alternative dioxin abatement technology can significantly inhibit the de-novo formation of PCDD/F on flyash deposits in the post-combustion zone of waste incinerators.

According to several authors, SO_2 sulphonates the phenolic precursors which prevent chlorination and bi-aryl synthesis, and promote the formation of sulphur analogues of PCDD/F (Gullett et al., 1992, Ogawa et al., 1996, Tuppurainen et al., 1998). In addition, Ke et al., (2010) suggested that SO_2 can sulphonate the copper catalysts resulting in the suppression of organic chlorine (C-Cl) formation. The main mechanism of inhibition was proposed to be the conversion of both CuO and $CuCl_2$ into non-reactive sulphate (Ryan et al., 2006; Ke et al., 2010). It is suggested that the inhibition is strongly based on the interaction between SO_2 and metallic catalysts such as CuO, $CuCl_2$, and $FeCl_2$ which are present in the flyash, and the inhibition mechanisms are temperature dependent. Based on the metal contents of the flyash sample used in this work including Cu and Fe, it would be reasonable to infer that their catalytic activities towards PCDD/F formation could have been reduced via possible sulphonation to metal sulphates.

4. Conclusions

A reference municipal waste incinerator flyash (BCR-490) was thermally treated under simulated flue gas with separate ammonia and SO_2 injections. The temperatures investigated were similar to post-combustion conditions of an incinerator to study the influence of these additives on PCDD/F formation. The results suggest that ammonia and sulphur dioxide can reduce the PCDD/F concentration from the solid phase more than that from the gas phase. No significant changes in congener profiles were observed with the two additives, however reduction of lower chlorinated PCDD in the solid phase occurred. Results also show that the inhibitory effects of these two gases were more prevalent on PCDD formation than on PCDF formation. Ammonia showed higher inhibitory ability on the formation of toxic PCDD/F congeners at 225 °C than at 375 °C. In contrast, SO_2 was more active at higher temperature than at the lower temperature. These observations suggest that the individual effects of these additives could be temperature-dependent.

It was found that the injection of gaseous ammonia into the flue gas could decrease the concentration of both PCDD and PCDF by 34-75% from the solid phase and by 21-40% from the gas phase. Converting the results to I-TEQ values, it could reduce the total I-TEQ values of PCDD and PCDF in the sum of the flyash and exhaust flue gas by 42 - 75% and 24 - 57%, respectively. The application of SO_2 led to substantial 99% and 93% reductions in the PCDD and PCDF concentrations, respectively in the solid phase. In the gas phase, the total reductions were 89% and 76% for PCDD and PCDF, respectively. Moreover, addition of SO_2 reduced the total I-TEQ value of PCDD and PCDF in the flyash and exhaust flue gas together by 60 - 86% and 72 - 82% respectively. The total reduction in the PCDD I-TEQ value was a minimum 58% at 225ºC and reached 84% at 375ºC. Also, for the PCDF congener, the total reduction in I-TEQ was 70% at 225 ºC and nearly 75% at 375 ºC.

While the gas-phase PCDD/F would have their origins from the solid phase (flyash) reactions involving solid-solid and gas-solid interactions, the higher percentage reductions observed in the solid phase here may suggest significant effects on these interactions by the presence of these additives. In essence, these results are supported by the inhibition mechanisms involving the ‘unavailability’ of the relevant metals, though present in the flyash, to catalyse PCDD/F formation. In this work, sulphur dioxide was more effective than ammonia in suppressing PCDD/F formation in flyash under the tested conditions.

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Figure Captions:

Figure 1: Schematic diagram of the experimental reactor for thermal treatment of flyash

Figure 2: Concentration profiles of the PCCD/F in the solid and gas phases after 96 h reaction at: (a) 225 ºC and (b) 375 ºC

Figure 3: Comparison of the efficiencies of NH_3 and SO_2 in reductions of PCDD/Fs toxic equivalency values from the solid and gas phases in relation to reaction temperature

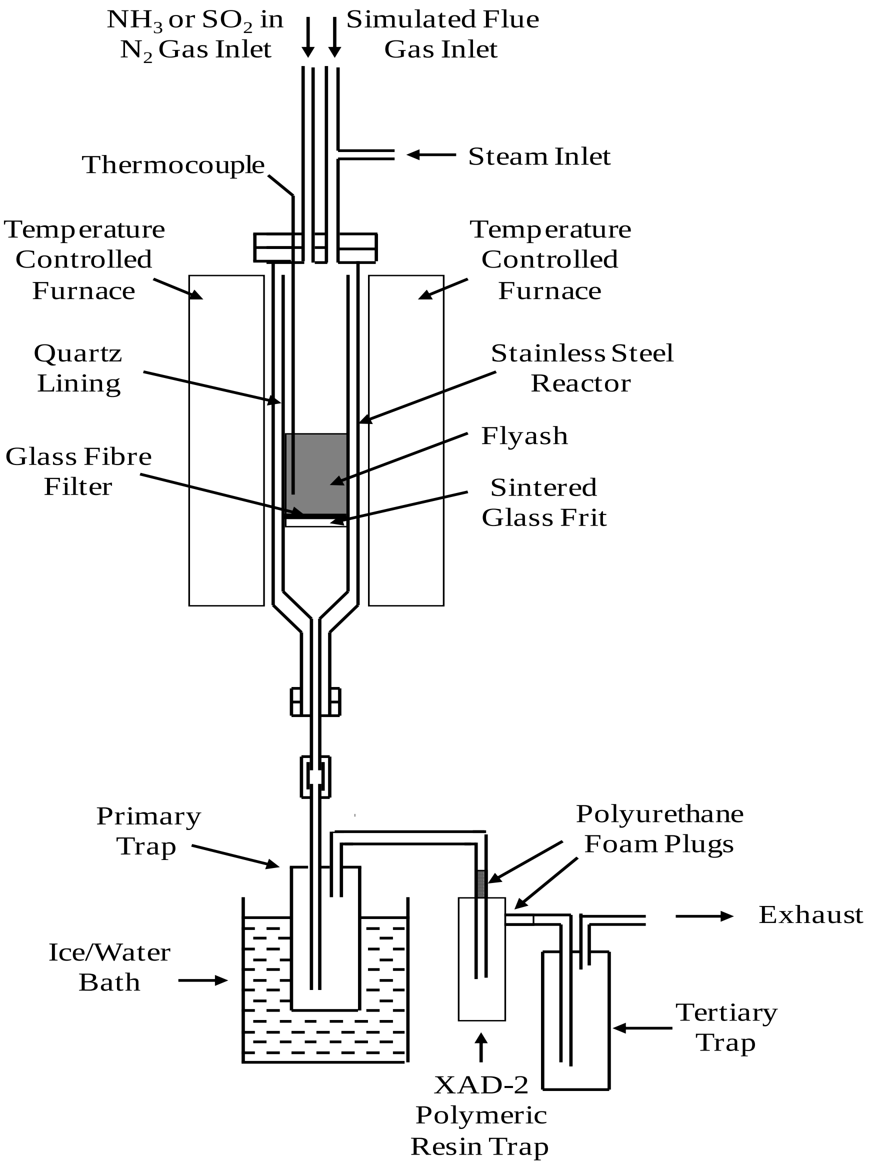

NH_3 or SO_2 in N_2 Gas Inlet
Simulated Flue Gas Inlet
Steam Inlet
Thermocouple
Temperature Controlled Furnace
Temperature Controlled Furnace
Quartz Lining
Stainless Steel Reactor
Flyash
Glass Fibre Filter
Sintered Glass Frit
Primary Trap
Polyurethane Foam Plugs
Exhaust
Ice/Water Bath
Tertiary Trap
XAD-2 Polymeric Resin Trap

Figure 1

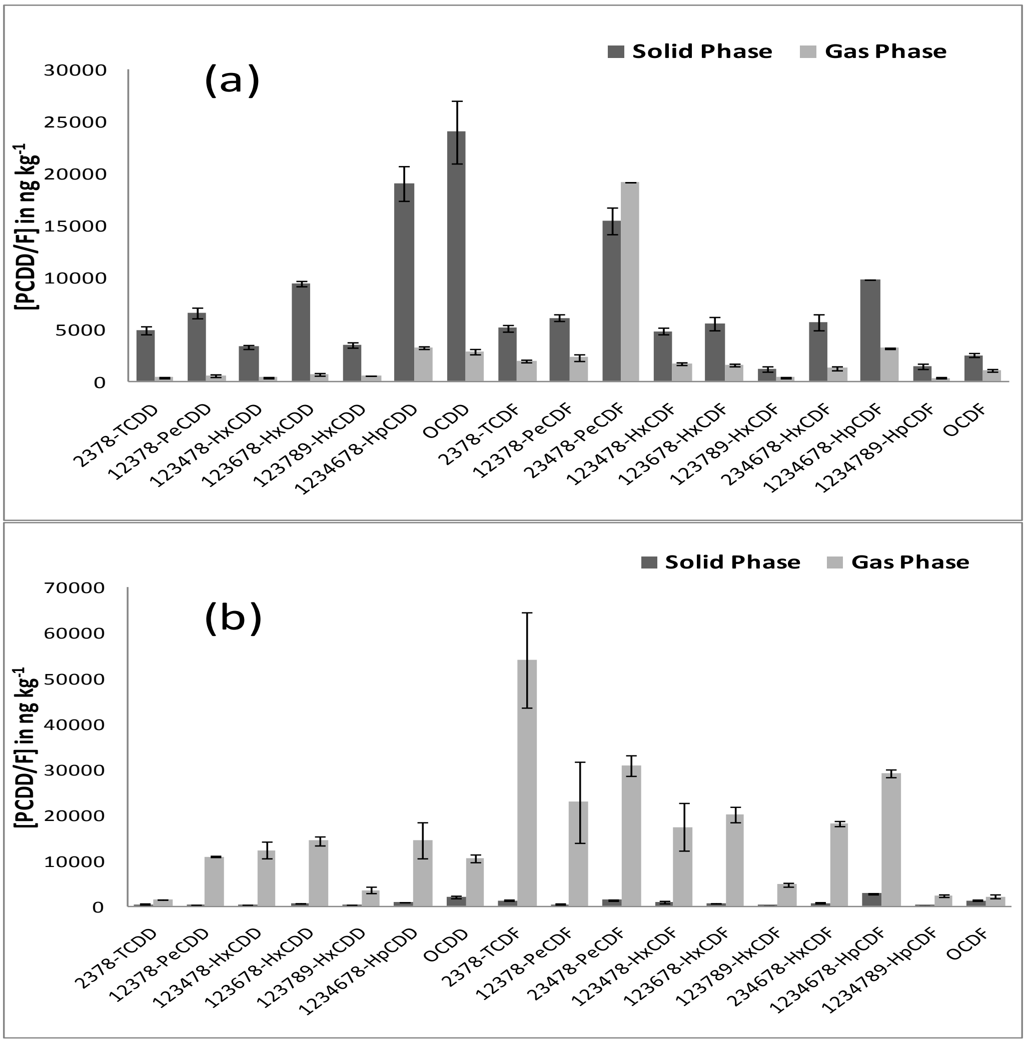
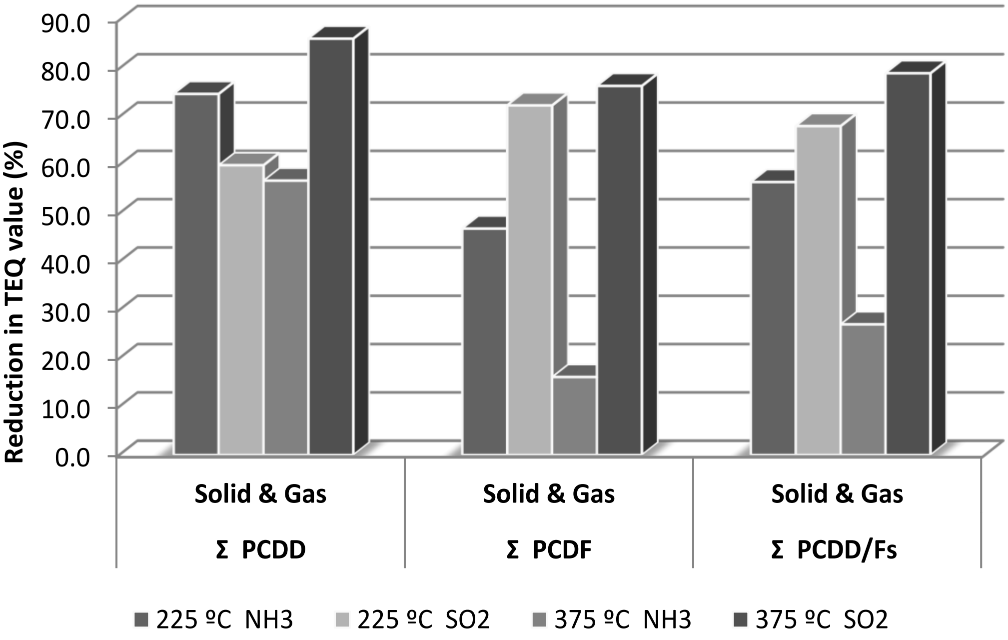

(a)
Solid Phase
Gas Phase
[PCDD/F] in ng kg^{-1}
30000
25000
20000
15000
10000
5000
0
2378-TCDD
12378-PeCDD
123478-HxCDD
123678-HxCDD
123789-HxCDD
1234678-HpCDD
OCDD
2378-TCDF
12378-PeCDF
23478-PeCDF
123478-HxCDF
123678-HxCDF
123789-HxCDF
234678-HxCDF
1234678-HpCDF
1234789-HpCDF
OCDF
(b)
Solid Phase
Gas Phase
[PCDD/F] in ng kg^{-1}
70000
60000
50000
40000
30000
20000
10000
0
2378-TCDD
12378-PeCDD
123478-HxCDD
123678-HxCDD
123789-HxCDD
1234678-HpCDD
OCDD
2378-TCDF
12378-PeCDF
23478-PeCDF
123478-HxCDF
123678-HxCDF
123789-HxCDF
234678-HxCDF
1234678-HpCDF
1234789-HpCDF
OCDF

Figure 2



90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
Reduction in TEQ value (%)
Solid & Gas
Σ PCDD
Solid & Gas
Σ PCDF
Solid & Gas
Σ PCDD/Fs
225 ºC NH3
225 ºC SO2
375 ºC NH3
375 ºC SO2

Figure 3

Table 1: Concentrations of PCDD/F in the unreacted flyash and in flyash reacted at 225 °C under simulated post-combustion zone conditions without and with the inhibitors

PCDD/Fs	**Certified value (ng kg-1)**	**This Study (ng kg-1)**	**[a]Total PCDD/F obtained after 96 h reaction at designated temperatures without and with the inhibitor**		
			225 °C (ng kg-1)		
			No inhibitor	**with NH_3**	**With SO_2**
2378-TCDD	169	161	5360 ± 340	616 ± 120	580 ± 80
12378-PeCDD	670	680	7170 ± 260	2290 ± 6	4830 ± 30
123478-HxCDD	950	975	3750 ± 280	1330 ± 9	2530 ± 40
123678-HxCDD	4800	4990	10200 ± 1100	4700 ± 460	4020 ± 320
123789-HxCDD	2840	2810	4080 ± 140	2050 ± 320	4430 ± 710
1234678-HpCDD	-	3160	22400 ± 1100	18900 ± 1400	28000 ± 2300
OCDD	-	5150	26900 ± 1800	22900 ± 1700	32300 ± 3000
Σ PCDD (ng I-TEQ kg-1)	**1700**	**1750**	**14600**	**3900**	**6790**
2378-TCDF	900	98	6620 ± 240	5810 ± 710	750 ± 80
12378-PeCDF	1710	1810	8460 ± 1000	5040 ± 380	6460 ± 360
23478-PeCDF	1850	2000	34700 ± 930	17000 ± 3100	6930 ± 1500
123478-HxCDF	2370	2650	6580 ± 1500	5080 ± 280	5810 ± 440
123678-HxCDF	2640	2970	7100 ± 1100	3740 ± 470	6090 ± 870
123789-HxCDF	340	360	1560 ± 620	400 ± 60	750 ± 90
234678-HxCDF	2470	2840	7000 ± 660	4450 ± 220	4890 ± 210
1234678-HpCDF	-	963	13100 ± 40	9880 ± 100	10200 ± 140
1234789-HpCDF	-	178	1810 ± 230	1240 ± 100	1480 ± 140
OCDF	-	155	3600 ± 90	4090 ± 620	5610 ± 810
Σ PCDF (ng I-TEQ kg-1)	**1900**	**2100**	**20800**	**10800**	**5730**
PCDD/PCDF (I-TEQ Ratio)	0.89	0.83	0.70	0.36	1.18

a = PCDD/F in both solid and gas phases

Table 2: Concentrations of PCDD/F in the unreacted flyash ash and in flyash reacted at 375 °C under simulated post-combustion zone conditions without and with the inhibitors

PCDD/Fs	**Certified value (ng kg-1)**	**This Study (ng kg^{-1})**	**[a]Total PCDD/F obtained after 96 h reaction at designated temperatures without and with the inhibitors**		
			375 °C (ng kg-1)		
			No inhibitor	**with NH_3**	**With SO_2**
2378-TCDD	169	161	1910 ± 110	983 ± 180	370 ± 70
12378-PeCDD	670	680	11200 ± 160	5260 ± 380	1820 ± 120
123478-HxCDD	950	975	12600 ± 1200	1920 ± 200	610 ± 70
123678-HxCDD	4800	4990	15000 ± 910	5660 ± 550	1370 ± 90
123789-HxCDD	2840	2810	3850 ± 500	2320 ± 210	40 ± 3
1234678-HpCDD	-	3160	15500 ± 2700	7070 ± 880	1520 ± 210
OCDD	-	5150	12600 ± 520	4350 ± 760	1030 ± 170
Σ PCDD (ng I-TEQ kg-1)	**1700**	**1750**	**16400**	**7300**	**2410**
2378-TCDF	900	938	55300 ± 7500	21000 ± 2700	1000 ± 90
12378-PeCDF	1710	1810	23400 ± 6300	27500 ± 4400	8340 ± 1400
23478-PeCDF	1850	2000	32200 ± 1100	30500 ± 1800	9730 ± 340
123478-HxCDF	2370	2650	18300 ± 3500	21400 ± 2600	7030 ± 940
123678-HxCDF	2640	2970	20900 ± 1200	19100 ± 2700	4890 ± 90
123789-HxCDF	340	360	4980 ± 400	2260 ± 350	890 ± 180
234678-HxCDF	2470	2840	19000 ± 290	14400 ± 1400	2380 ± 210
1234678-HpCDF	-	963	32100 ± 210	24700 ± 1500	5490 ± 290
1234789-HpCDF	-	178	2550 ± 230	3450 ± 320	570 ± 40
OCDF	-	155	3740 ± 150	4260 ± 570	1110 ± 170
Σ PCDF (ng I-TEQ kg-1)	**1900**	**2100**	**29500**	**24700**	**6760**
PCDD/PCDF (I-TEQ Ratio)	0.89	0.83	0.56	0.30	0.36

a = PCDD/F in both solid and gas phases

Table 3: Effect of NH_3 on PCDD/F formation in relation to treatment temperature

	% Reductions of PCDD/F during NH_3 Injection			
	225 °C		**375 °C**	
	Solid Phase	**Gas Phase**	**Solid Phase**	**Gas Phase**
2378-TCDD	90.8 ± 0.8	60.8 ± 0.4	86 ± 11	36.5 ± 7.1
12378-PeCDD	70.7 ± 2.3	36.8 ± 12	73.7 ± 14	52.4 ± 5.3
123478-HxCDD	64.2 ± 3.7	67.4 ± 6.4	80 ± 16	84.9 ± 2.6
123678-HxCDD	55 ± 6.8	38.8 ± 16	81.3 ± 1.5	61.6 ± 10
123789-HxCDD	47.6 ± 9.5	63.4 ± 2.4	90.6 ± 9.1	36.4 ± 2.0
1234678-HpCDD	8.6 ± 4.2	57 ± 6.8	53.7 ± 1.0	54.4 ± 7.2
OCDD	12.3 ± 3.8	36.6 ± 11	36.7 ± 2.3	71 ± 6.6
2378-TCDF	28.2 ± 7.5	-7.3 ± 3.9	-40.2 ± 9.3	64.4 ± 5.8
12378-PeCDF	42.1 ± 0.4	35.7 ± 13	12 ± 2.4	-18.1 ± 3.1
23478-PeCDF	52.1 ± 10	47.6 ± 1.8	30.2 ± 5.9	4.1 ± 2.1
123478-HxCDF	28.9 ± 9.2	5.9 ± 2.6	66.5 ± 1.7	-21 ± 0.6
123678-HxCDF	48.6 ± 0.7	43 ± 4.9	59.1 ± 2.7	6.9 ± 3.5
123789-HxCDF	74.6 ± 5.3	73.2 ± 21	79.8 ± 13	53.7 ± 5.4
234678-HxCDF	37.5 ± 7.5	31.4 ± 5.5	42.3 ± 8.1	23.4 ± 1.7
1234678-HpCDF	20.9 ± 1.3	34.8 ± 7.0	45.2 ± 6.0	21.1 ± 0.2
1234789-HpCDF	33.5 ± 10	23.8 ± 6.4	34.7 ± 3.9	-39.4 ± 10
OCDF	-36.7 ± 11	-19.7 ± 7.9	28.8 ± 5.2	-55.5 ± 8.9

Table 4: Effect of SO_2 on PCDD/F formation in relation to treatment temperature

	% Reductions of PCDD/F during SO_2 Injection			
	225 °C		375 °C	
	Solid Phase	**Gas Phase**	**Solid Phase**	**Gas Phase**
2378-TCDD	94.1 ± 0.6	29.9 ± 2.5	100 ± 0.0	74.4 ± 0.5
12378-PeCDD	48.1 ± 7.8	-151 ± 31	100 ± 0.0	83.3 ± 2.2
123478-HxCDD	43 ± 5.6	-55.1 ± 6.5	100 ± 0.0	95.1 ± 0.5
123678-HxCDD	75.1 ± 3.8	-131 ± 23	100 ± 0.0	90.5 ± 0.5
123789-HxCDD	-5.61 ± 7.2	-26.2 ± 6.5	100 ± 0.0	99.1 ± 0.2
1234678-HpCDD	-24.3 ± 4.8	-28.4 ± 5.6	98.5 ± 0.5	89.7 ± 1.6
OCDD	-19.4 ± 2.4	-26.3 ± 3.1	90.9 ± 1.6	92 ± 0.5
2378-TCDF	94.3 ± 0.5	69.3 ± 4.9	57.1 ± 5.0	99.1 ± 0.1
12378-PeCDF	58.6 ± 6.7	-69.6 ± 11	100 ± 0.0	63.6 ± 2.1
23478-PeCDF	87.6 ± 8.6	74 ± 0.9	97.2 ± 1.3	68.5 ± 2.4
123478-HxCDF	44.8 ± 4.3	-81.2 ± 3.9	100 ± 0.0	59.7 ± 0.7
123678-HxCDF	45.8 ± 8.4	-96.7 ± 12	100 ± 0.0	75.8 ± 1.4
123789-HxCDF	57.7 ± 6.8	32.8 ± 7.9	100 ± 0.0	81.5 ± 1.4
234678-HxCDF	62.6 ± 1.8	-116 ± 11	100 ± 0.0	87 ± 2.4
1234678-HpCDF	40.8 ± 2.1	-34.2 ± 8.5	90.9 ± 2.0	82.1 ± 0.6
1234789-HpCDF	32.1 ± 7.0	-42.3 ± 11	100 ± 0.0	76.2 ± 2.2
OCDF	-27.9 ± 8.3	-119 ± 25	80.7 ± 0.8	62.8 ± 6.1