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PCDD/Fs Inhibition by Sludge Decomposition Gases: Effects of Sludge Dosage, Treatment Temperature and Oxygen Content

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ABSTRACT

Sludge decomposition gases (SDG) have been identified as potential PCDD/F-inhibitors, since they contain high concentrations of NH_3 and SO_2 as well as various unidentified N- and S-compounds. The effects of sludge dosage, its treatment temperature and oxygen content on PCDD/Fs suppression were observed during test runs using a model fly ash (MFA) system, generating high chlorinated PCDD/Fs. The experiments were carried out in two parts: a first set with SDG of undefined composition, and a second with injection of NH_3 and SO_2 combined in three different concentration ratios. It was observed that the SDG evolving from dried sludge (DS) could suppress the formation of 2,3,7,8-substituted PCDD/Fs even with very high efficiency (> 99%), both in weight units and in I-TEQ units. Such suppression was somewhat stronger for PCDD than PCDF. It was also found that 300°C might be a suitable sludge decomposition temperature when using SDG as suppressant in PCDD/Fs inhibition. Moreover, the oxygen content only slightly influenced upon the suppression capabilities. The results revealed that SO_2 was more effective than NH_3 in suppressing PCDD/Fs formation, with suppression efficiencies of 61.9% and 38.6%, respectively. Remarkably, the formation of OCDD/Fs was inhibited least and even further formation could occur when both NH_3 and SO_2 were injected together as simulated flue gas. The results exposed that NH_3 and SO_2 might be the primary PCDD/Fs suppressants resulting from mild thermal decomposition of sludge. However, further parameters should be evaluated and adjusted before SDG could be used in large-scale applications.

Keywords: Inhibition; NH_3; SO_2; PCDD/Fs; Sludge decomposition gases.

INTRODUCTION

The amount of municipal solid waste (MSW) generated in China is increasing impressively, from 148.6 million ton in 2003 to 170.8 million ton in 2012, in line with the figures for economic development (National Bureau of Statistics of China, 2004 and 2013). MSW Incineration is already widely applied in MSW treatment in China: in 2012 over 25% of the MSW was disposed of by burning. However, incineration is still controversial for it might cause secondary pollution, in particular by the emission and eventual deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) (Olie *et al.*, 1977; Chen *et al.*, 2008; Gao *et al.*, 2009; Ngoc and Schnitzer, 2009; Xu *et al.*, 2009a, b). Much attention is paid to such PCDD/Fs because of their potential environmental impacts (Suzuki *et al.*, 2005; Shih *et al.*, 2006; Lee *et al.*, 2007; Zheng *et al.*, 2008). In most thermal processes, including incineration and pyrometallurgy, dioxins are mainly formed by heterogeneous reactions, in which fly ash is the key catalyst carrier. Numerous studies have been performed on the inhibition of PCDD/Fs by chemical suppressants, especially N- or S-containing compounds, such as NH_3, $(NH_4)_2SO_4$, urea and SO_2 (Takacs and Moilanen, 1991; Addink *et al.*, 1996; Raghunathan and Gullett, 1996; Samaras *et al.*, 2000; Kuzuhara *et al.*, 2005; Pandelova *et al.*, 2007; Kasai *et al.*, 2008). The suppressants are added to the raw MSW or injected into incinerator flue gases. In addition, Hunsinger *et al.* (2007) designed a system on recirculation of SO_2 for suppression of PCDD/F and that this avoids the continuous addition of sulphur or nitrogen compounds. However, the cost of supplying such substances is tangible, so finding cheap and effective suppressants has been a topical subject for R&D initiatives.

Sludge decomposition gases (SDG), evolving from mild thermal decomposition of sewage sludge, contain NH_3 and SO_2 as well as other, unidentified N- and S-compounds (Lindbauer *et al.*, 1992; Hong *et al.*, 2009; Lu *et al.*, 2013; Chen *et al.*, 2014). It was observed that these SDG are able to suppress up to 69.5% of the PCDD/Fs amount and 78.7%

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of TEQ (Yan *et al.*, 2012), yet the dosage, temperature, moisture and oxygen content during sludge decomposition could all affect the release characteristics of actively inhibiting N- and S-compounds. When the sludge decomposition temperature was raised from 140°C to 170°C, the emission rate of NH_3 could expand 120% (Deng *et al.*, 2009). When sludge was treated at 260°C, Chun *et al.* (2012) observed that the concentration of NH_3 was ca. three times higher than that at 225°C (Chun *et al.*, 2012). Accordingly, the oxygen content of the carrier gas used to heat sludge could influence upon the emission characteristics of N- and S-compounds (Cusidó and Soriano, 2011; Lu *et al.*, 2013; Widman *et al.*, 2013). Therefore, the eventual suppression of PCDD/Fs and I-TEQ by vapours generated during sludge decomposition could be influenced by sludge dosage, its treatment temperature, and the moisture and oxygen content of the decomposition gases.

The suppression effect of NH_3 and SO_2 was studied before by several researchers. Adding compounds containing either N or S at times led to relatively limited inhibitory effects (Ruokojärvi *et al.*, 2004; Pandelova *et al.*, 2007; Hajizadeh *et al.*, 2012; Wu *et al.*, 2012). For instance, only 70% of PCDD/Fs inhibition efficiency was achieved using 390 ppm SO_2 as an additive (Ogawa *et al.*, 1996), whereas 1% w/w of amidosulfonicacid (ASA) would lead to 96% reduction of PCDD/Fs.

In metallurgical processes sulfur is less desirable. British Steel patented the use of urea in inhibiting PCDD/F formation. A series of nitrogen compounds were tested in the suppression of PCDD/F formation from highly reactive filter dust, sampled from an iron ore sintering belt: triethanolamine (TEA; 0.2, 0.5, 1 and 5%), $Ca(OH)_2$ (2 and 5%), NaOH (2 and 5%), urea (1%) and ammonia (200 ppm) added as aqueous ammonia to the gas phase. The best effect was reached with strongly basic substances, yet gaseous ammonia was found to be ineffective (Hell *et al.*, 2000b). In another study simple housekeeping measures combined with suppression successfully reduced the PCDD/F-emissions arising from a manganese ore sintering belt (Brown *et al.*, 2003).

This paper examines the changes in concentration and profile of the toxic 2,3,7,8-substituted PCDD/F congeners obtained while using model fly ash (MFA) samples in suppression tests related to the dosage, temperature and oxygen content during sludge decomposition. Most importantly, these experiments also established the appropriate conditions to inhibit the formation of PCDD/Fs efficiently. In addition, the effects of injecting NH_3 together with SO_2 into the flue gas on the concentration of PCDD/F congeners have been considered. The results could confirm the important role of both NH_3 and SO_2 in the suppression of PCDD/Fs by SDG.

MATERIALS AND METHODS

Experimental Materials

In this study a synthetic model fly ash was used to simulate PCDD/Fs formation. This model fly ash was chosen with similar characteristics to the fly ash produced from MSWI (Hell *et al.*, 2000a) to allow an unequivocal interpretation of eventual changes of fly ash state and composition. This model fly ash is composed of (in wt.%) 91.8% of SiO_2, 3% of activated carbon, 5% of NaCl and 0.2% of $CuCl_2$, corresponding to a fly ash load of ca. 3.1% Cl, 0.1% Cu, and 3% C.

The sludge samples were collected from a municipal wastewater treatment plant in Shanghai. The raw sludge samples were dried for 24 h in an oven at 105°C, and the resulting sample is then referred to as dried sludge (DS). The dried samples have a high N content (4.87 wt.%) and a low S content (0.79 wt.%). Their moisture content and ultimate or elemental analysis are presented in Table 1.

Experimental Set-up

Thermal decomposition of the DS samples were accomplished using the experimental set-up described in Fig. 1. The same apparatus was also used for the PCDD/Fs' suppression experiments. It comprises a tubular furnace consisting of three sections a, b, and c (0.5 m for each section) and featuring independent heaters and temperature controllers to maintain the desired temperature profile. The sludge and the model fly ash were each separately located, between two quartz cotton layers situated in a short quartz tube and in the internal quartz tube respectively. The external and internal diameter of the quartz reactor tube was 45 and 30 mm. The simulated flue gas (300 mL/min; 12% O_2 in N_2) was divided into two parts (Gas A and Gas B). Gas A consisted of nitrogen (264 mL/min) yet it featured different contents of oxygen when it was used to prepare the sludge decomposition gases (SDG) used as suppressant. Gas B contained the oxygen necessary to conduct a PCDD/F generation test at a fixed concentration of 12 vol.%. The SDG and Gas B were well mixed at the end of the short quartz tube and then these mixed gases passed through the fixed bed of model fly ash, to inhibit the formation of PCDD/Fs. The experimental test conditions are listed in Table 2 and are further explained in the Experimental Design (see 2.4.). In general, laboratory experiments with model fly ashes not necessarily reflect the situation in real application.

The experimental procedure was established to take into account the unsteady evolution of volatile suppressants during the additional heating of dried sludge. Before each experiment, this DS was preheated for 3.5 min up to 300°C (or to 350°C and 250°C, for test runs B-4 and C-4, respectively) and from then on the suppressant gases were directed to flow over the model fly ash. After 15 minutes a second portion of sludge is pushed into the heating zone, so that a new surge of suppressant gases is produced.

PCDD/Fs Analysis

In these experiments, we only analyzed for seventeen 2,3,7,8-substituted PCDD/Fs congeners. The cleanup procedure of PCDD/Fs samples was conducted according to the USEPA 1613 method (U.S EPA, 1994). The identification and quantification of PCDD/Fs were performed by HRGC/HRMS using a 6890 Series gas chromatograph (Agilent, USA) coupled to a JMS-800D mass spectrometer (JEOL, Japan). A DB-5ms (60 m × 0.25 mm I.D., 0.25 μm film thickness) capillary column was used for separation of

Table 1. Moisture content and ultimate analysis of the dried sludge sample before the experiment (wt. %).

	Moisture	Carbon	Hydrogen	Nitrogen	Sulfur
Dry Sludge (DS), Shanghai	7.09	24.75	3.72	4.87	0.79

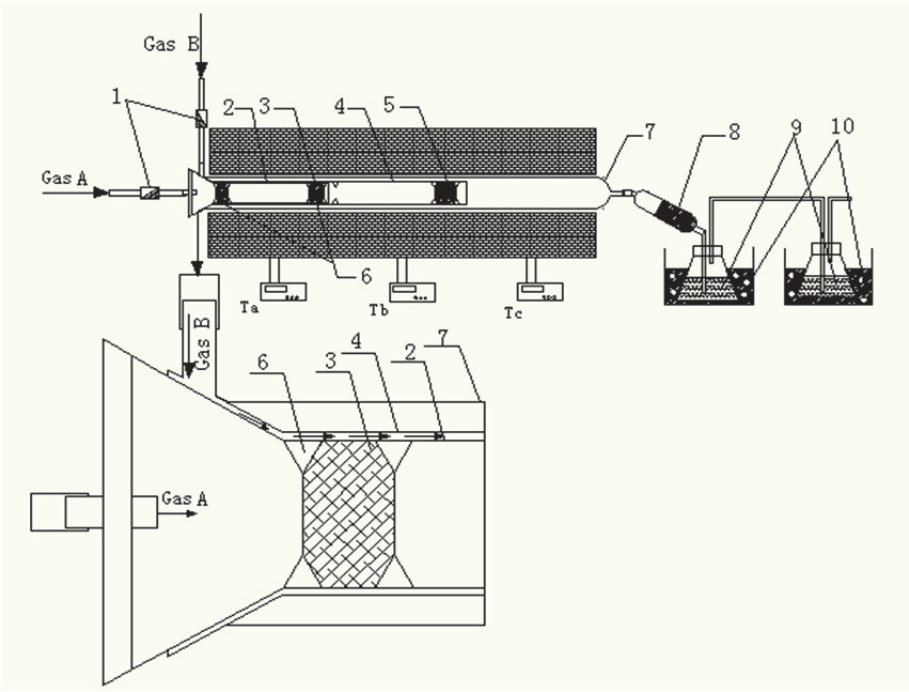

Fig. 1. Experimental system for conducting the sludge drying and inhibition experiments. (1: Mass flow meter, 2: Short quartz tube, 3: Dry sludge, 4: Internal quartz tube, 5: Model fly ash, 6: Quartz rod, 7: External quartz tube, 8: XAD-Ⅱ resin, 9: Toluene, 10: Ice bath).

Table 2. Experimental design conditions.

No	Inhibitor	Ta	O_2	No.	Inhibitor	Ta	O_2
A	none	-	12%	B-1	2 g DS	300°C	0%
B-2	2 g DS	300°C	6%	B-3	2 g DS	300°C	12%
B-4	2 g DS	350°C	12%	C-1	1 g DS	300°C	0%
C-2	1 g DS	300°C	6%	C-3	1 g DS	300°C	12%
C-4	1 g DS	250°C	12%	D-1	900 ppm SO_2 + 100 ppm NH_3	300°C	12%
D-2	100 ppm SO_2 + 900 ppm NH_3	300°C	12%	D-3	500 ppm SO_2 + 500 ppm NH_3	300°C	12%

Legend: T_a and refer to the treatment conditions during the preparation of the Sludge Drying Gases SDG.
The conditions of the de novo tests (A) and concomitant suppression tests are: 300 °C, 50 min, 12 vol. % O_2.

the different PCDD/Fs congeners. The GC temperature program was optimized as follows: splitless injection of 1 μL at 150°C, initial oven temperature of 150°C for 1 min, then increased at 25 °C/min to 190°C, finally increased at 3 °C/min to 280°C and held for 20 min at the final temperature. All tests were conducted in duplicate, except for the tests A, which were repeated five times; the arithmetic average of the results was further used in our analysis of suppression.

Experimental Design

Test A is considered to be a blank test, i.e. a test without the addition of suppressing sludge-derived S- and N-compounds, supplied as part of the carrier gas stream during the *de novo* PCDD/Fs formation tests on model fly ash.

Then, in the series B, and C sludge samples were tested as suppressants: the series B and C compare a double SDG dosage (B) to a single (C), whereas series D tests the effect of specific mixes of NH_3 and SO_2 in suppressing PCDD/F formation (cf. Table 2); for samples DS (Shanghai dried sludge, high in N, low in S) eight distinct test conditions were established, namely B (1 g + 1 g DS, per 2 g of model fly ash) and C (0.5 g + 0.5 g DS, per 2 g of model fly ash). The tests use three different treatment temperatures (250°C, 300°C and 350°C) to heat the DS, and also the oxygen content of the carrier gas used during sludge decomposition is varied (0, 6, and 12 vol.%). However, the oxygen content of the simulated flue gas flowing over the model fly ash was always 12 vol.%.

Lastly, in order to confirm the inhibition effect of NH_3 and SO_2 and study the inhibition mechanism of SDG, three distinct conditions are tested, namely D. D-1 and D-2 focus on investigating the inhibition effect of NH_3 and SO_2 separately. The purpose of D-3 is to study the eventual synergetic effect of NH_3 and SO_2 further.

In the experiments A the amount of PCDD/Fs generated was determined separately in both the gas phase and the residue. Since the PCDD/Fs largely remained in the model fly ash (ca. 99.9%), however, the fly ash and gas phase were analyzed together as a lumped sample in the further tests.

RESULTS AND DISCUSSION

PCDD/F Synthesis and Inhibition

Experiment A was conducted five times to confirm the total PCDD/Fs produced from the model fly ash. The average concentration of total PCDD/Fs was 2534 ± 222 ng/g (or 77.7 ± 32.9 ng I-TEQ/g). The PCDD/F congener distribution is dominated by the PCDF, with 70.0 ± 2.9% of the total PCDD/F, and also by OCDF (41.3 ± 4.1%) and OCDD (25.2 ± 1.65%). The best defined congeners are OCDD (± 9%) and 1234678-HpCDF (± 10%). Unexpectedly, the least reproducible congener was 23478-PeCDF, which explains the width of the confidence interval of the I-TEQ-value. The blank experiment showed an unusually high weight average degree of chlorination, with values of 7.81 for Cl-PCDD and 7.31 for Cl-PCDF. Such a remarkably high average level of chlorination is typical for model fly ash incorporating $CuCl_2$ as a catalyst.

The I-TEQ values of the sludge samples were always quite low (Stevens *et al.*, 2001; Lu *et al.*, 2012) and almost no PCDD/Fs would desorb from sludge and enter with the SDG into the fly ash model system.

During the suppression tests with SDG (experiment series B and C) the reduction efficiencies of 2,3,7,8-substituted PCDD/Fs always exceeded 80%; especially experiments B-4, with a reduction of 99.9% in the PCDD/Fs concentration and of 99.2% in the I-TEQ value scored highly (Table 2). The high concentration of NH_3 and SO_2 may account tentatively for this result, yet the effect of unidentified S- and N-compounds cannot be excluded. Similar suppression effects could be achieved bythe injection of, e.g., sulfur dioxide, ammonia, dimethylamine, and methylmercaptan on particle-phase PCDD/Fs (Ruokojärvi *et al.*, 1998). These results also show that several factors of influence, including the sludge dosage, and the temperature and oxygen content during sludge decomposition, could directly or indirectly affect the suppression efficiencies obtained for the PCDD/Fs.

The least favorable results were obtained during the suppression tests with gaseous NH_3 and SO_2 solely (experiments D). Suppression efficiency values computed on a basis of PCDD/Fs were quite low during these tests, especially for D-3, namely 0.3%. However, in some experiments also a dramatic increase in chlorination level occurred, as shown in Table 2. Accordingly, the values of I-TEQ decreased from 77.7 ng I-TEQ/g to less than 19.0 ng I-TEQ/g with the combined addition of gaseous NH_3 and SO_2. This result shows that a disappointing effect on the total amount of PCDD/Fs may be accompanied by a remarkable decrease in the toxicity equivalent I-TEQ.

PCDD/F Inhibition by SDG

Effect of DS Dosage

The amount of inhibitor applied could greatly influence the suppression effect of PCDD/Fs. For instance, 0.5 wt.% of sodium ammonium hydrogen phosphate (NAHF) reduced the particle-phase PCDD/Fs by 40% and this value would be raised to 90% when 1.0 wt.% of NAHF was added. Furthermore, the reduction efficiencies of urea on PCDD/Fs formation at 0.1%, 0.5% and 1.0% of the fuel feed were 64%, 75% and 90%, respectively (Ruokojärvi *et al.*, 2001). Most importantly, the efficiency of reducing PCDD/Fs formation by addition of sulfur is strongly influenced by the S/Cl mole ratio (Lindbauer *et al.*, 1992, Raghunathan and Gullett 1996, Duo and Leclerc 2004), and thus the DS dosage could further influence the suppression efficiency of PCDD/Fs.

In these experiments the suppression efficiency was monitored after addition of 1 + 1 g (B-1, B-2 and B-3) or 0.5 + 0.5 g (C-1, C-2 and C-3) DS heated at 300°C. The three B-experiments attained a suppression efficiency of 95.9 to 99.94% (PCDD/Fs) or of 98.84 to 99.33% (I-TEQ). Even when reducing the DS amount from 1 + 1 g to 0.5 + 0.5 g, the PCDD/F inhibition efficiency was still above 80%.

Fig. 2 shows the suppression efficiency of the seventeen 2,3,7,8-substituted PCDD/Fs.

In almost all above cases the suppression efficiency was somewhat stronger for PCDD than for PCDF, except for B-2 and B-4, where essentially equally high values of > 99.9% were attained. This trend was consistent with the results reported by Chang *et al.* (2006), who added elemental sulfur to the fly ash from a municipal waste incinerator, which was reacted at 300°C in a gas stream. However, when added to the flue gas sulfur has a greater inhibitory effect on PCDF formation than on PCDD formation.

In general, NH_3 was the primary PCDD/F suppressant resulting from DS decomposition and a clear decrease in the concentration of both PCDD and PCDF congeners occurred when NH_3 was used as an additive.

No characteristic changes in congener distribution would be observed in earlier studies (Addink *et al.*, 1996; Hajizadeh *et al.*, 2012). In this study this congener distribution is of paramount importance: because of the very high average chlorination level of PCDD and PCDF any deviation from full octa-chlorination assumes great importance.

The blank test sample is composed of 30.0 ± 2.9% PCDD and 70.0 ± 2.9% PCDF, forming the balance.

The B- and the C-series are leaner in PCDD, since suppression of PCDD is stronger. Thus, the composition of PCDD/Fs becomes: 22.4 ± 8.3% PCDD (B-tests), 23.8 ± 2.6% PCDD (C-tests) and 25.3 ± 2.8% PCDD, with the balance PCDF.

The congener profiles of the 17 toxic 2,3,7,8-substituted PCDD/Fs (weight units) are shown in Figs. 3(a) and 3(b). The PCDD of the A-samples are entirely dominated by OCDD (84.3 ± 3.5%) and 1,2,3,4,6,7,8-HpCDD (13.3 ± 3.0%); for the PCDF the two most dominant congeners are OCDF

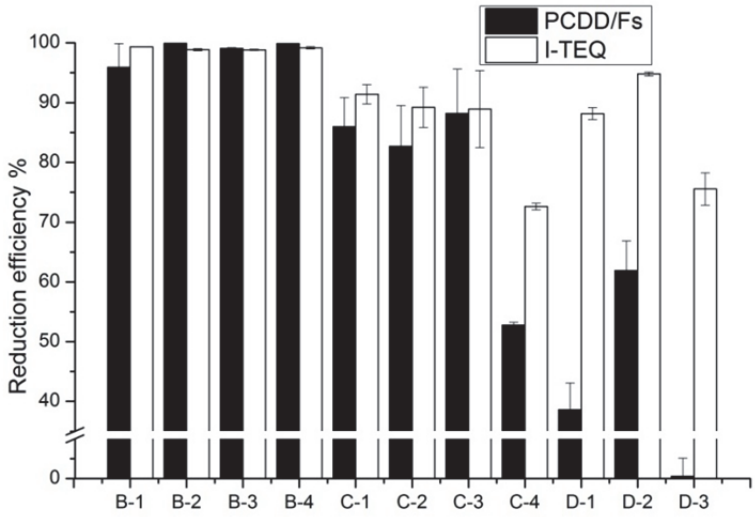

Fig. 2. Suppression efficiency of the seventeen 2,3,7,8-substituted PCDD/Fs, in wt. units and in I-TEQ values.

(58.9 ± 3.7%) and 1,2,3,4,5,7,8-HpCDF (16.9 ± 3.3%). The PCDD-fingerprints of the B- and C-series resemble well those established for the A-profile, yet the D-series sees an even stronger preponderance of OCDD (95.8 ± 3.5%) among the PCDD. The B- and C-series show strong scatter within the PCDF-profiles affecting mainly the relative amounts of OCDF and 1,2,3,4,5,7,8-HpCDF. Moreover, there is a promoting effect in the C-series for 2,3,7,8-TCDD when compared with A-samples and B-series.

The B-series shows the deepest suppression of the I-TEQ value, with values ranging from 98.84 to 99.33%. During the C-series the SDG is halved, reducing the suppression efficiency to ca. 90% (test runs C-1 to C-3). Even the D-series still attains impressive inhibition of the I-TEQ values (Table 3).

Effect of DS Decomposition Temperature

The inhibitory effects of SDG on PCDD/Fs formation could be due to many distinct factors, including the type, the concentration, and the emission characteristics of N- and S-compounds (Furrer *et al.*, 1998; Stieglitz *et al.*, 1998). Since the composition of DS is complex and the evolving S- and N-compounds unidentified and possibly highly variable, the decomposition temperature might influence the ability of SDG in suppressing PCDD/Fs formation.

The results of Yan *et al.* (2012) indicated that decomposition at 200°C was high enough for PCDD/F inhibition (Yan *et al.*, 2012). In general, the higher the decomposition temperature applied, the shorter the emission time period of N- and S-compounds would last. Comparison between the experiments B-3 and B-4 shows that the suppression effects of PCDD/Fs when DS was heated at 350°C were still stronger than at 300°C. A comparison between the experiments C-3 (300°C) and C-4 (250°C) also shows better results for the higher decomposition temperature. Considering energy savings and emission reduction, the sludge decomposition temperature should not be selected too high, and thus 300°C was selected as the most appropriate decomposition temperature.

Comparison between B-3 (C-3) and B-4 (C-4) also shows an increase in chlorination levels of both PCDD and PCDF when the sludge decomposition temperature was changed: the fraction of OCDD and OCDF increased (see Figs. 3(a) and (b)). In the presence of NH_3 the suppression of lower chlorinated PCDDs was larger than for highly chlorinated ones (Hajizadeh *et al.*, 2012). Hence, these results were in agreement with some previously reported results using sulfur compounds as inhibitors (Lee *et al.*, 1998). However, no clear trend was found in the reduction of PCDF congeners in the presence of NH_3. Conversely, SO_2 suppression effects were found to be higher for high chlorinated PCDF (Pandelova *et al.*, 2007). The results in this study revealed that the reduction of low substituted congeners with high toxic equivalency value were more favorable at 250°C and 350°C than at the sludge decomposition temperature at 300°C.

A comparison between B-3 (C-3) and B-4 (C-4) also shows an increase in chlorination levels of both PCDD and PCDF when the sludge decomposition temperature was varied: the fraction of OCDD and OCDF increased (see Figs. 3(a) and 3(b)). In the presence of NH_3 the suppression of lower chlorinated PCDDs was larger than for highly chlorinated ones (Hajizadeh *et al.*, 2012). Hence, these results were in agreement with some previously reported results using sulfur compounds as inhibitors (Lee *et al.*, 1998). However, no clear trend was found in the reduction of PCDF congeners in the presence of NH_3. Conversely, SO_2 suppression effects were found to be higher for high chlorinated PCDF (Pandelova *et al.*, 2007). The results in this study revealed that the reduction of low substituted congeners with high toxic equivalency value were more favorable at 250°C and 350°C than at the standard sludge decomposition temperature at 300°C.

By comparison and analysis, we found that sludge could emit more PCDD/Fs suppression gases, such as NH_3, SO_2 and HCN, in case the decomposition temperature was raised step by step. However, further work is needed to establish the best mode of temperature rise in terms of PCDD/F inhibition results.

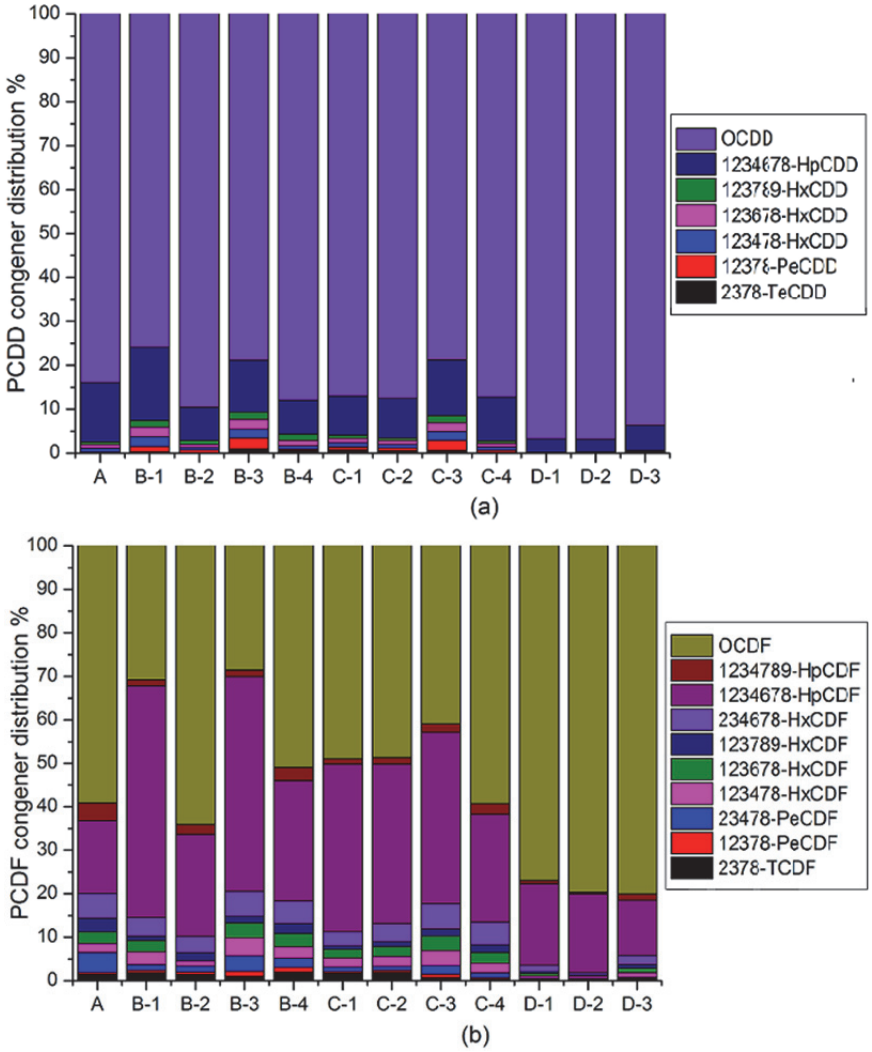

Fig. 3. Congener profiles of the PCDD (a) and PCDF (b) without and with various inhibitors.

Effect of Oxygen Content during DS Decomposition

The emission characteristics of these compounds liberated during DS decomposition could be affected by the oxygen content and thus the suppression efficiencies would be varied. In an industrial context it is plausible to use the residual heat of flue gas to treat the sludge and thus to produce a large amount of SDG. In addition, after a deep decomposition the sludge will act as a fuel supplement: dry sludge has the same calorific value as lignite and a low chlorine content (Werther and Ogada, 1999; Francisca Gómez-Rico *et al.*, 2005).

The sludge decomposition atmosphere also could influence the emission characteristics of PCDD/Fs suppression gases, e.g., by a partial oxidation of active suppressants. In general, 100% N_2 enhanced the emission of NH_3 and the emission of SO_2 increased under the simulated flue gas condition.

As described in Fig. 2, no significant and systematic changes were observed in the PCDD/F suppression efficiencies when the oxygen content of the sludge decomposition atmosphere was varied (0%, 6% and 12%), especially for 1 + 1 g DS. Comparison between C-1, C-2 and C-3 showed that C-1 and C-3 had a stronger suppression effect on PCDD/Fs than C-2, revealing that DS heated in 6% O_2 of carrier gas may release much less N- and S-compounds.

The result for the PCDD/F congeners was very different, yet without any clear trends in the reduction of their concentration in the presence of SDG. Interestingly, the chlorination level of PCDD/Fs when DS heated in 6% of decomposition atmosphere was higher than that of 0% and 12%. As for I-TEQ value, no obvious differences were observed, and the suppression efficiencies of them were ca. 90%.

These tests with SDG can be concluded with the following statements:

1. A deep reduction (99.9%) of PCDD/F formation was realized during two duplicated test runs: B-2 and B-4. These tests feature a somewhat lower reduction of the I-TEQ values, of 98.9 and 99.2%, respectively.

2. The identity and the nature of the active suppressants are still unidentified. Two plausible contenders for such a role are gaseous NH_3 and SO_2.

PCDD/F Inhibition by Gaseous NH_3 and SO_2

During the previous tests SDG has proved to be a highly efficient suppressant of PCDD/F-formation. Since the

precise composition of SDG is basically unknown and also varies with the origins, composition and thermal treatment conditions of the sludge three supplemental tests were also conducted using a mixture of 1000 ppm NH_3 and SO_2 of known composition: 900 ppm NH_3 and 100 ppm SO_2, 100 ppm NH_3 and 900 ppm SO_2, and 500 ppm NH_3 and 500 ppm SO_2.

Injection of 900 ppm NH_3 and 100 ppm SO_2

The results obtained with (mainly) NH_3 injection are presented in Table 3. The suppression efficiency recorded on PCDD/Fs was 38.7%, which was well within the range (34–75% for the solid phase and 21–40% for the gas phase) reported by Hajizadeh *et al.* (2012). Interestingly, suppression was much stronger for PCDD than PCDF: 54.9% and 31.6%, respectively. Moreover, when compared with the base case both chlorination levels increased, with a significant decrease in I-TEQ value as a consequence. The reduction of lower chlorinated congeners was greater than that for high chlorinated ones, for both PCDD and PCDF congeners (see Figs. 3(a) and 3(b)). For example, 1,2,3,7,8-PeCDD and 1,2,3,7,8-PeCDF were reduced by 92.9% and 93.8% respectively, whereas OCDD and OCDF reduced by 48.1% and 11.0% respectively. These results were also comparable with the results reported by Ruokojärvi *et al.* (1998), who found that the total PCDD/F concentration was reduced between 42% and 78%. However, varying the NH_3 concentration and the temperature of the fly ash would affect the PCDD/Fs congener distribution. So results from this work showed some difference in PCDD/F congeners with other similar works.

In contrast with the addition of SDG, 2,3,4,7,8-PeCDF is not the major contributor to I-TEQ, since it accounts for only 13.8%, whereas the percentage of 2,3,4,6,7,8-HxCDF and 1,2,3,4,6,7,8-HpCDF are 19.5% and 24.6% respectively. In addition, PCDF is still the major contributor to I-TEQ, which accounts for 93.8% of total I-TEQ. This could be mainly attributed to the exceptionally high levels of PCDF in terms of I-TEQ.

Injection of 100 ppm NH_3 and 900 ppm SO_2

The suppression efficiency of PCDD/Fs was found to be 61.9%, which was within the range (42–75% for the solid phase and 24–57% for the gas phase) reported by Hajizadeh *et al.* (2012). It also agrees with the work of Shao *et al.* (2010), who found that the addition of SO_2 to the inlet gas of a model ash treatment test at 350°C could reduce the PCDD/F levels by about 90%, with a S/Cl ratio of 0.25. In this test, the S/Cl ratio exceeded 20, but it is unclear why the reduction of PCDD/Fs was far lower than in the results of Shao *et al.* (2010). Furthermore, SO_2 was more effective than NH_3 in suppressing PCDD/Fs formation, consistent with the results reported by Hajizadeh *et al.* (2012).

In contrast with the addition of 900 ppm NH_3, the suppression effects on PCDD and PCDF were quite close, 66.0% and 60.2%, respectively. Moreover, the reduction efficiencies of OCDD and OCDF were only 60.7% and 46.4%, whereas the average values of suppression efficiencies of the lower chlorinated exceed 90%. Therefore, the I-TEQ

Table 3. Results regarding the suppression of PCDD and PCDF.

Item	A	B-1	B-2	B-3	B-4	C-1	C-2	C-3	C-4	D-1	D-2	D-3	Unit
DS dosage	0	2	2	2	2	1	1	1	1	0	0	0	DS per 2 g MFA
PCDD	761	21.5	0.502	2.72	0.656	77.5	102	61.2	301	343	259	679	ng PCDD/g MFA
PCDF	1773	82.1	1.14	20.8	1.79	278	337	235	896	1212	706	1847	ng PCDF/g MFA
PCDD/PCDF	42.9	26.2	44.0	13.1	36.6	27.9	30.3	26.0	33.6	28.3	36.7	36.7	%, PCDD/Fs
ΣPCDD/Fs	2534	103	1.64	23.5	2.44	357	439	296	1197	1555	965	2526	ng PCDD-F/g MFA
PCDD/Fs reduction, %	0	95.9	99.9	99.1	99.9	86.0	82.7	88.2	52.8	38.7	61.9	0.284	%, PCDD/Fs
I-TEQ	77.7	0.521	0.884	0.905	0.643	6.69	8.37	8.61	21.27	9.20	4.05	19.0	ng I-TEQ/g MFA
I-TEQ reduction, %	0	99.3	98.9	98.8	99.2	91.4	89.2	88.9	72.6	88.2	94.8	75.6	%, I-TEQ
Cl-PCDD	7.81	7.67	7.86	7.65	7.82	7.81	7.82	7.67	7.84	7.96	7.96	7.93	Weight average level
Cl-PCDF	7.31	7.11	7.46	7.01	7.25	7.33	7.30	7.19	7.44	7.73	7.77	7.73	of chlorination.

value decreased by 94.8%, even more than with the SDG produced from 0.5 + 0.5 g DS. In addition, 1,2,3,4,6,7,8-HpCDF was also the major contributor to I-TEQ, which accounted for ca. 31.7%.

Injection of 500 ppm NH_3 and 500 ppm SO_2

Remarkably, during the two tests with a joint injection of 500 ppm NH_3 and 500 ppm SO_2 a negative reduction for the sum PCDD/Fs was observed. Although a clear decrease in the concentrations of PCDD/Fs occurred when either 500 ppm NH_3 or 500 ppm SO_2 was injected (Ruokojärvi *et al.*, 1998; Ke *et al.*, 2010; Wu *et al.*, 2012), only 0.3% of PCDD/Fs reduction was achieved in these experiments when they were injected together. The experiments were conducted in duplicate and the results were well reproducible, with values for the standard variation of 11% for PCDD, 8%% for PCDF and 16% for I-TEQ.

Strangely enough, a strong reduction was observed on all lower chlorinated PCDD, ranging from 83.9% for 2378-TeCDD to 62.3% for 1234678-HpCDD, yet only 0.4% for OCDD. The situation was fairly similar for PCDF, with strong reductions for lower chlorinated PCDF, culminating in a 92.5% reduction for 23478-PeCDF and lowest for the two main PCDF congeners: only 20.8% for 1234678-HpCDF and a negative reduction of –41.1% for OCDF. Also, the reductions on the lower chlorinated congeners were comparable with the suppression effects of NH_3 and SO_2. Thus, the suppression efficiency of total I-TEQ would reach 75.6%.

Thus this test has led to a very strange situation: although the total amount of suppression calculated on PCDD/Fs was negligible, the effect on I-TEQ was quite rewarding. The following two hypotheses may help to explain this strange result. One might be that the acidic effect of SO_2 and the basic effect of NH_3 and that equal amounts neutralizes somehow. Another possible reason is that the concentrations of NH_3 and SO_2 were not large enough to suppress the activity of formation of PCDD/Fs in our fly ash model system. Most importantly, the abatement of SO_2, NH_3 and other nitrogen and sulphur compounds need to be considered if such gases are used for suppression of PCDD/F formation. Therefore levels of 500 or 900 ppm addition might have consequences for the flue gas cleaning a therefore cost.

CONCLUSIONS

Five *de novo* tests were conducted using model fly ash (MFA) to establish the average level of PCDD/F formation under standard conditions (300°C, 12 vol.% O_2). Such standard PCDD/F formation was suppressed during the following eleven inhibition tests, each conducted *in duplo,* and using either sludge decomposition gases (SDG) rich in nitrogen- and sulfur compounds, or else a mixture of NH_3 and SO_2 as suppressant. The sludge dosage, and the treatment temperature and oxygen content during sludge decomposition might influence the emission characteristics of N- and S-compounds, which are effective PCDD/Fs suppressants. The most suitable experimental condition identified in the paper was probably: using 0.5 + 0.5 g of dried sludge DS, heated at 300°C, to treat 2 g of MFA. The oxygen content of the decomposition atmosphere did not play an important role in PCDD/Fs suppression. Clear reductions of PCDD/Fs were also observed with the injection of NH_3 and SO_2.

Obviously, the suppression by gaseous NH_3 and SO_2 passes over a poisoning or other form of neutralization of the $CuCl_2$ catalyst active in converting carbon into PCDD/Fs. A first step in such a deactivation process is adsorption. It seems likely that larger S- and N-molecules easier condense and adsorb onto the reacting system than do NH_3 and SO_2.

According to the relevant literature the S/Cl-ratio is of paramount importance. Moreover, the signature of the PCDD/F would be very similar in the original standard system and its inhibited counterparts. The results obtained in this study demonstrate that minor differences in fingerprint may be very consequential in the results obtained, in particular when these are expressed in I-TEQ units.

Further work is needed to evaluate the PCDD/Fs suppression effect on pilot scale tests in incinerators, to apply this inhibition technique using SDG to real MSWI process.

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SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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Supplementary Materials

Table 1

The congener profiles of 2,3,7,8-substituted PCDD/Fs (pg/g).

	A(1)	A(2)	A(3)	A(4)	A(5)	B-1(1)	B-1(2)
2,3,7,8-TCDD	312	237	110	230	226	1	120
1,2,3,7,8-PeCDD	1788	1385	1160	2496	1916	1	536
1,2,3,4,7,8-HxCDD	5707	3963	5448	8248	6242	4	942
1,2,3,6,7,8-HxCDD	4971	2899	6265	8126	5868	9	920
1,2,3,7,8,9-HxCDD	4218	2698	4257	6864	4785	5	650
1,2,3,4,6,7,8-HpCDD	91752	53135	110499	137060	103110	70	7089
OCDD	665628	535409	645831	661686	638900	709	31882
2,3,7,8-TCDF	26570	17839	16076	32078	24936	63	2950
1,2,3,7,8-PeCDF	8275	5441	5434	10827	7792	23	955
2,3,4,7,8-PeCDF	192268	120199	26516	50532	82985	66	1995
1,2,3,4,7,8-HxCDF	40743	27398	33700	40259	36394	46	4809
1,2,3,6,7,8-HxCDF	45929	33326	46751	53453	47703	0	4256
1,2,3,7,8,9-HxCDF	51451	31097	65666	64508	55441	93	1544
2,3,4,6,7,8-HxCDF	93851	60751	113601	122629	101133	121	6966
1,2,3,4,6,7,8-HpCDF	271694	293599	347842	279440	294961	467	86989
1,2,3,4,7,8,9-HpCDF	73721	44416	80065	83649	73359	51	2284
OCDF	1218499	1044571	837872	985741	1047962	1344	49134
∑PCDDs	774275	599726	773570	842709	832860	799	42139
∑PCDFs	2023001	1678637	1573524	1723116	1865040	2272	161881
∑PCDD/Fs	2797376	2278362	2347095	2547826	2533712	3071	204021

	B-2(1)	B-2(2)	B-3(1)	B-3(2)	B-4(1)	B-4(2)	C-1(1)
2,3,7,8-TCDD	0	0	14	38	0	7	630
1,2,3,7,8-PeCDD	3	4	68	68	3	2	674
1,2,3,4,7,8-HxCDD	3	3	53	54	6	4	1006
1,2,3,6,7,8-HxCDD	2	5	73	49	10	6	980
1,2,3,7,8,9-HxCDD	5	4	51	41	11	8	693
1,2,3,4,6,7,8-HpCDD	30	47	431	212	101	0	7070
OCDD	358	540	3271	1018	707	445	55359
2,3,7,8-TCDF	19	12	158	252	39	32	4348
1,2,3,7,8-PeCDF	8	7	207	291	21	16	1002
2,3,4,7,8-PeCDF	15	16	729	753	46	31	2480
1,2,3,4,7,8-HxCDF	12	14	920	776	64	29	4069
1,2,3,6,7,8-HxCDF	0	0	832	608	77	34	3608
1,2,3,7,8,9-HxCDF	17	25	423	215	57	25	1291
2,3,4,6,7,8-HxCDF	34	52	1512	880	121	64	6211
1,2,3,4,6,7,8-HpCDF	238	295	14293	6249	653	341	75768
1,2,3,4,7,8,9-HpCDF	22	31	432	196	81	30	1535
OCDF	619	837	9483	2380	1156	670	653484
∑PCDDs	401	602	3962	1482	838	473	66412
∑PCDFs	985	1289	28990	12599	2315	1273	165697
∑PCDD/Fs	1386	1891	32952	14079	3153	1746	232109

	C-1(2)	C-2(1)	C-2(2)	C-3(1)	C-3(2)	C-4(1)	C-4(2)
2,3,7,8-TCDD	442	534	602	491	241	429	203
1,2,3,7,8-PeCDD	406	558	700	2075	908	1934	1418
1,2,3,4,7,8-HxCDD	563	707	998	1718	810	2633	1942
1,2,3,6,7,8-HxCDD	514	666	963	1740	808	2614	2030
1,2,3,7,8,9-HxCDD	482	438	816	1488	562	1876	1419
1,2,3,4,6,7,8-HpCDD	6716	6231	12180	12133	3984	29490	30770
OCDD	79419	68264	109640	80981	18837	262493	261875
2,3,7,8-TCDF	4967	5107	7840	2409	615	2560	3031
1,2,3,7,8-PeCDF	1211	1065	2082	3148	1071	3493	3157
2,3,4,7,8-PeCDF	3628	2790	3504	7560	1809	10896	9315
1,2,3,4,7,8-HxCDF	7423	4992	10270	12832	3208	19969	19664
1,2,3,6,7,8-HxCDF	7569	4340	11099	12654	3330	22665	21820
1,2,3,7,8,9-HxCDF	3134	1277	6026	6795	808	14729	16768
2,3,4,6,7,8-HxCDF	11654	6381	22089	23610	3711	43991	49446
1,2,3,4,6,7,8-HpCDF	138508	87083	159798	138706	46713	225008	219448
1,2,3,4,7,8,9-HpCDF	5199	1738	8873	7999	1010	20731	23827
OCDF	206674	73763	254086	169938	22599	522095	540120
∑PCDDs	88541	77398	125899	100626	26149	301469	299657
∑PCDFs	389967	188535	485667	385653	84874	886138	906595
∑PCDD/Fs	478508	265933	611566	486279	111023	1187607	1206253

	D-1(1)	D-1(2)	D-2(1)	D-2(2)	D-3(1)	D-3(2)
2,3,7,8-TCDD	0	0	10	0	14	59
1,2,3,7,8-PeCDD	156	115	140	95	634	651
1,2,3,4,7,8-HxCDD	297	207	226	287	921	1628
1,2,3,6,7,8-HxCDD	286	189	202	270	827	1405
1,2,3,7,8,9-HxCDD	215	145	147	187	539	1248
1,2,3,4,6,7,8-HpCDD	12353	8476	9261	5557	30628	47153
OCDD	357428	305942	206099	295433	592670	679724
2,3,7,8-TCDF	3571	3078	1458	1877	6313	9582
1,2,3,7,8-PeCDF	593	372	393	410	1280	1945
2,3,4,7,8-PeCDF	2751	2331	1019	1346	4864	7606
1,2,3,4,7,8-HxCDF	7357	5968	3480	3903	16409	19596
1,2,3,6,7,8-HxCDF	8086	5731	2700	0	17134	21194
1,2,3,7,8,9-HxCDF	6382	4845	689	873	14794	17864
2,3,4,6,7,8-HxCDF	19884	16017	3156	4086	31452	45513
1,2,3,4,6,7,8-HpCDF	230238	222983	116122	140414	251004	216098
1,2,3,4,7,8,9-HpCDF	10372	7917	2333	2683	22904	32756
OCDF	1007930	857771	491393	632742	1591585	1365032
∑PCDDs	370736	315074	216085	301828	626262	734867
∑PCDFs	1297165	1127013	622743	788334	1957738	1737186
∑PCDD/Fs	1667900	1442087	838829	1090162	2583970	2469052