



Thermal removal of PCDD/Fs from medical waste incineration fly ash – Effect of temperature and nitrogen flow rate

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ABSTRACT

The fly ash used in this study was collected from a bag filter in a medical waste rotary kiln incineration system, using lime and activated carbon injection followed by their collection as mixed fly ash. Experiments were conducted on fly ash in a quartz tube, heated in a laboratory-scale horizontal tube furnace, in order to study the effect of temperature and nitrogen flow rate on the removal of PCDD/Fs. Results indicated that in this study PCDD/Fs in the fly ash mostly were removed and desorbed very little into the flue gas under thermal treatment especially when the heating temperature was higher than 350 °C, and dechlorination and destruction reactions took important part in the removal of PCDD/Fs. However, in terms of flow rate, when flow rate was higher than 4 cm s⁻¹, destruction efficiency of PCDD/Fs decreased dramatically and the main contributors were P₅CDF, H₆CDF and H₇CDF desorbed to flue gas, the PCDD/Fs in the fly ash decreased with enhanced flow rate.

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1. Introduction

In modern municipal or hazardous solid waste incinerators, the boiler has been well designed, and combustion conditions have been well are controlled. Air pollution control devices (APCDs) are also employed to reduce polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) emissions from the stack. PCDD/Fs emissions from stack have to be well controlled and must be under the Europe limit of 0.1 ng I-TEQ Nm⁻³. However, PCDD/Fs not only occur from phase transfer from the gas phase to the solid phase (fly ash), but also from the increasing total amount of PCDD/Fs, mainly contributed by the “de novo” reaction of fly ash when passing through the post-combustion zone (Stanmore, 2004; Chen et al., 2008a). Moreover, because of the “memory effect”, PCDD/Fs are formed from fly ash continuously even if the incinerator is shutdown when fly ash deposits in duct wall or APCDs is not removed in time (Zimmermann et al., 2001).

It is reported that removing fly ash deposits from the flue duct walls has been shown to reduce the emissions of PCDD/Fs (Wevers and de Fré, 1998). Nevertheless, fly ash accounts for 70% to 90% of the total PCDD/Fs released from an incinerator (Abad et al., 2001), and the problem emerges due to the toxicity of fly ash. In some countries fly ash is considered as hazardous waste, which could not be land-filled directly. Solidification provides a method for fly ash pretreatment before landfill, and result indicates that leachability of PCDD/Fs can be reduced, but the solidification capability

depends on characteristic of fly ash (Kim and Lee, 2002; Hsi et al., 2007).

Another promising method is thermal treatment which takes place under inert gas condition at low temperatures. Vogg and Stieglitz (1986) found that under oxidative conditions, a temperature of 400–600 °C was needed to decompose PCDD/Fs; however, PCDD/Fs could be decomposed effectively when under inert gas condition. In the studies followed, identical results were obtained under N₂ or static gas conditions (Hagenmaier et al., 1987; Addink et al., 1995a; Lundin and Marklund, 2005; Cunliffe and Williams, 2007). However, thermal treatment was only a laboratory skill to study fly ash problem, and no researcher has developed a large scale or pilot scale equipment to eliminate PCDD/Fs in fly ash. In China, the definition of toxicity of different fly ashes is not clear, and a large quantity of fly ash from waste incinerators is landfilled either after solidification treatment or directly. In the near future, the management of fly ash will become stricter, and thermal treatment will be a promising method to resolve the fly ash problem.

Medical waste is dangerous and infectious, and needs special treatment even after burning. The characteristics of medical waste are different from municipal solid waste in terms of components such as paper, plastics and textile, and after burning, fly ashes also differ because of the incineration conditions and APCDs, and in most cases are higher in PCDD/Fs, PCBs and other POPs (Oh et al., 1999; Stanmore and Clunies-Ross, 2000). Researchers reported that fly ash from medical waste incinerator has a higher level of PCDD/Fs than that from municipal solid waste incinerators and electrical power plants (Chen et al., 2008b). In recent years, our research has been dedicated to the incineration of medical wastes,

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pollutant control and PCDD/Fs destruction and some achievements have been obtained (Lu et al., 2007; Yan et al., 2009). In this study, thermal treatment was introduced to decompose PCDD/Fs in fly ash collected from a medical waste incinerator, temperature and flow rate parameters were discussed influencing decompose of PCDD/Fs. Finally, guidance for fly ash from medical waste incinerator thermal treatment was obtained to minimize the concentration of PCDD/Fs.

2. Materials and methods

2.1. Fly ash sample

Fly ash was collected from a medical waste rotary kiln incinerator. In this system, medical waste is combusted first in a rotary kiln and the residue passed to a secondary combustor (burnout). After combustion, the flue gas is rapidly quenched by water to keep the temperature between 180 °C and 200 °C, avoiding reformation of PCDD/Fs. The quenching tower is unique for medical waste incineration. Operated with lime injection, acid gas is adsorbed; then PCDD/Fs in the gas phase and solid phase are adsorbed by activated carbon (AC) spray and particles by a bag filter. The mixed lime, AC and fly ash are collected by the bag filter. Finally, the gas from stack satisfies emission control regulations. The fly ash used for the experiments is the mixture taken from the bag filter. The elemental composition and other characteristics of fly ash collected from the bag filter are listed in Table 1.

2.2. Thermal treatment reactor

The experiments were conducted in a laboratory-scale horizontal tube furnace with quartz tube as a reactor. Approximately 0.5 g fly ash was used in each experiment. Before each experiment condition, the tube was flushed with N₂ longer than 10 min, making sure that atmospheric air and remained eluent were expelled. During the experiment, the whole system was inserted with nitrogen gas, and each process lasted for 60 min. During temperature parameter influenced experiment, the gas flow rate was stabilized at 200 mL min⁻¹ (2 cm s⁻¹), and temperatures of 300 °C, 350 °C, 400 °C were used; when the flow rate were changed, the temperature was stabilized at 350 °C, and flow rates used were 200 mL min⁻¹ (2 cm s⁻¹), 300 min⁻¹ (3 cm s⁻¹) and 400 min⁻¹ (4 cm s⁻¹). During the experiment, the organic compounds in the flue gas were adsorbed by XAD-2 resin and a toluene scrubbing solution. A blank experiment was used for accuracy. When the experiment ended, the glass trap which contained XAD-2 resin was covered with aluminum foil, and the toluene scrubbing solution was collected in brown bottle, also thermal treated fly ash

Table 1
Properties of the medical waste incinerator fly ash.

Properties	Properties	Properties	
C (wt.%)	8.96	Mg (wt.%)	0.10
H (wt.%)	1.98	Ni (mg kg ⁻¹)	10.1
O (wt.%)	25.7	Pb (mg kg ⁻¹)	107
N (wt.%)	0.12	Zn (wt.%)	0.33
S (wt.%)	0.20	Cr (mg kg ⁻¹)	ND
P (wt.%)	0.03	As (mg kg ⁻¹)	1.33
Cl (wt.%)	8.70	Hg (mg kg ⁻¹)	63.0
Cu (wt.%)	0.06	BET surface area (m ² g ⁻¹)	65.8
Na (wt.%)	10.4	Micropore area (m ² g ⁻¹)	21.4
K (wt.%)	0.36	External surface area (m ² g ⁻¹)	44.4
Ca (wt.%)	1.49	Pore volume (cm ³ g ⁻¹)	0.07
Al (wt.%)	0.08	Micropore volume (cm ³ g ⁻¹)	0.01
Fe (wt.%)	0.11	Mean pore radius (nm)	4.29
Cd (mg kg ⁻¹)	12.1	ND: Not detected	

was collected after cooled. Samples collected were stored in a refrigerator before analysis.

2.3. Analysis

Thermally treated fly ash and gas phase adsorbed samples were transferred to the glass thimble of the Soxhlet extractor and spiked with a mixture of ¹³C-labeled PCDD/Fs internal standards which were supplied by Wellington Laboratories, Canada. The spiked samples were extracted for 24 h with 250 mL toluene. A rotary evaporator concentrated the extract to 1–2 mL approximately, prior to the cleanup process. After concentration, a labeled cleanup standard was spiked into the extract, which was then cleaned using different methods. The extract should be treated again when using the extract was still colored.

Cleanup of samples were done using conventional manual chromatography columns including a multi-silica gel column, an alumina column and a Florisil column. After cleanup, the extract was concentrated again and transferred to a vial. Then, the remaining solvent in the vial was reduced to about 20 μL in a gentle stream of nitrogen. A ¹³C-labeled PCDD/Fs recovery standards mixture was spiked prior to HRGC/HRMS analysis.

The analysis was performed by HRGC/HRMS on a 6890 Series gas chromatograph (Agilent, USA) and coupled to a JMS-800D mass spectrometer (JEOL, Japan). A DB-5 ms (60 m × 0.25 mm I.D., 0.25 μm film thickness) capillary column was used for separation of the PCDD/Fs congeners. The GC temperature program and mass spectrometer were operated as described by Chen et al. (2008b). The detailed quantitative determination of PCDD/Fs was according to US EPA method 1613. Tetra- to octachlorinated PCDD/Fs were measured in this study.

The credibility of PCDD/Fs data was assured by adding internal standards mixture, purification standards mixture, and injection standards mixture before Soxhlet extraction, purification and analysis process respectively. Data analysis demonstrated that, the recovery rates of each internal standard were between 66% and 90%, which was accord with the recovery standard of 40% to 130%.

3. Results and discussion

3.1. Temperature influenced removal of PCDD/Fs in fly ash

The original concentration of PCDD/Fs in fly ash from medical waste incinerator is shown in Table 2. The total concentration of PCDD/Fs were 836 000 ng kg⁻¹, this is much higher than that of municipal solid waste incinerator fly ash literatures referred (Chen et al., 2008b; Lundin and Marklund, 2008). The I-TEQ concentration and WHO2005-TEQ concentration were a little different of 19 000 ng I-TEQ kg⁻¹ and 19 700 ng WHO2005-TEQ kg⁻¹, respectively, which were due to different TEQ factor of 1, 2, 3, 7, 8-P₅CDD, O₈CDD and O₈CDF, and 2, 3, 4, 7, 8-P₅CDF was the main contributor. Nowadays, 2, 3, 4, 7, 8-P₅CDF becomes the dominant I-TEQ contributor in the emissions from municipal solid waste and hazardous waste incinerators (Fiedler et al., 2000) or in the fly ashes of different sources (Chen et al., 2008b). It is obvious that the PCDDs/PCDFs ratio is much lower than 1 and it might due to improved incineration. Modern municipal solid waste incinerators tend to produce more PCDFs than PCDDs (Ryu et al., 2005), and some old incinerators show PCDDs/PCDFs ratio above 1 (Stieglitz and Vogg, 1987).

After thermal treatment under N₂ atmosphere, PCDD/Fs remained in fly ash was reduced dramatically in terms of tetra- to octachlorinated PCDD/Fs (Table 2), the total concentration of PCDD/Fs decreased from 836 000 ng kg⁻¹ to 8430, 2490 and 2350 ng kg⁻¹ at the temperature of 300 °C, 350 °C and 400 °C,

Table 2
Concentration of PCDD/Fs congeners at different heating temperatures (ng kg^{-1}).

Congeners	Original fly ash	300 °C		350 °C		400 °C	
	Solid phase	Solid phase	Gas phase	Solid phase	Gas phase	Solid phase	Gas phase
T ₄ CDD	10 700	ND	41.3	54.8	688	ND	613
P ₅ CDD	27 500	352	34.9	ND	418	ND	469
H ₆ CDD	22 400	ND	14.7	ND	49.4	ND	15.8
H ₇ CDD	54 400	ND	130	ND	ND	ND	ND
O ₈ CDD	38 500	ND	169	ND	182	ND	210
Total PCDDs	154 000	352	390	54.8	1340	ND	1310
T ₄ CDF	89 000	3640	487	1560	1240	1394	1130
P ₅ CDF	153 000	1280	61.5	294	414	519	731
H ₆ CDF	208 000	1340	160	350	440	271	84.7
H ₇ CDF	183 000	1820	327	231	392	169	159
O ₈ CDF	48 800	ND	ND	ND	ND	ND	ND
Total PCDFs	682 000	8080	1040	2440	2490	2350	2100
Total PCDD/Fs	836 000	8430	1430	2490	3820	2350	3410
I-TEQ	19 000	110	19.0	50.2	22.7	72.3	60.1
WHO2005-TEQ	19 700	110	18.9	50.2	22.6	72.3	59.9

ND: not detected, the detection level is 0.01 ng kg^{-1} , the same to the following data.

respectively. PCDD/Fs removal ability boosted with the increase of temperature especially when the temperature reached 350 °C. With respect to PCDDs, when the temperature was 300 °C, all of congeners except for P₅CDD were under detection limit, and the concentration of P₅CDD was decreased to 352 ng kg^{-1} . Dechlorination behavior was found at 350 °C when T₄CDD was again increased to 54.8 ng kg^{-1} , however, no P₅CDD was detected, it was suggested that some of P₅CDD might be dechlorinated to T₄CDD. When the temperature was 400 °C, no PCDDs were detected. With respect to PCDFs, the same removal trend was detected, high chlorinated PCDFs such as P₆CDD and H₇CDD decreased much more than T₄CDD and P₅CDD, which was also due to dechlorination behavior. However, much more PCDFs was detected than PCDDs, it was mainly because of more PCDFs than PCDDs in the original fly ash. Misaka et al. (2006) also found that 0.06% and 0.03% PCDD/Fs of that in original fly ash were detected when the temperature were 252 °C and 377 °C respectively under vacuum atmosphere with N₂, which was also contributed to dechlorination/hydrogenation (DCH) reactions (Hagenmaier et al., 1987). Stieglitz and Vogg (1987) showed that destruction process was favored at temperatures above 350 °C. However, if the treatment time is long enough, destruction of PCDD/Fs may be favored at temperatures around 300 °C or even 260 °C (Weber et al., 1999; Stach et al., 2000). Yet the treatment temperature is shown to be more important than treatment time in low temperature thermal treatment, the removal efficiencies by variation of treatment temperature were 2–10 times higher than that by variation of treatment time (Song et al., 2008). The phenomenon of PCDD/Fs removal from the fly ash under different temperatures suggests that 300 °C is enough for PCDD/Fs elimination in the fly ash, and when the temperature increases, the elimination trend will be more significant.

The PCDD/Fs desorbed from fly ash and then was adsorbed or absorbed by XAD-2 and toluene under thermal treatment has also been detected (Table 2). The PCDD/Fs desorbed to gas phase was low of 1430 ng kg^{-1} at 300 °C, and increased to 3820 ng kg^{-1} and 3410 ng kg^{-1} at 350 °C and 400 °C respectively. However, the desorbed I-TEQ of PCDD/Fs increased with the increase of heating temperature. For PCDD/Fs congeners, the increase of temperature did not enhance the total removal of PCDD/Fs, it was seen that desorption behavior was enhanced especially when the temperature was turned to 350 °C from 300 °C, however, no significant difference was seen from 350 °C to 400 °C, suggesting that 350 °C is a suitable temperature for PCDD/Fs removal. It seems that low chlorinated PCDD/Fs suffered much more from desorption behavior, tetra- and penta- chlorinated PCDD/Fs increased much more than higher

chlorinated PCDD/Fs when the temperature increased to 350 °C from 300 °C. Cunliffe and Williams (2007) also found that the desorbed PCDD/Fs congeners profile was mainly mono- to tri- chlorinated PCDD/Fs resulting from dechlorination of high chlorinated PCDD/Fs. It was thought that dechlorination and then decomposition of PCDD/Fs in fly ash contributed the most part of PCDD/Fs removal; however, higher vapor pressure of the lower chlorinated PCDD/Fs such as tetra- and penta- chlorinated PCDD/Fs former mentioned at higher temperature also ease the desorption progress (Chang et al., 2006), it might be the reason PCDD/Fs increased in the desorbed gas phase when the heating temperature was higher.

Chlorination degrees of PCDD/Fs in the solid phase of fly ash and the gas phase of flue gas at different heating temperatures are analyzed (Fig. 1). It was found that chlorination degrees decreased both in the solid phase and gas phase with thermal treatment and increasing heating temperature, which implied the dechlorination reaction of PCDD/Fs, and the desorbed PCDD/Fs was also influenced by dechlorination reaction. However, PCDDs was much more susceptible than PCDFs under experimental thermal condition. It has been suggested that dioxins in the fly ash are more susceptible to dechlorination than the furans at relative low temperatures (Addink et al., 1995b), which was explained later by Lundin and Marklund (2008) from chemical stability of PCDDs and PCDFs. Whereas, ratio of PCDDs/PCDFs shows different between solid phase and gas phase, decreasing trend was seen in the fly ash when the heating temperature increased, however, in the gas phase increasing trend was seen at the same experimental conditions. The decrease of PCDDs/PCDFs in the fly ash was due to the more susceptible dechlorination capability of dioxins than furans as former mentioned; and the increase of PCDDs/PCDFs in the flue gas was mainly due to the decrease of PCDFs at the higher temperature.

The total reduction rates of PCDD/Fs including concentration, I-TEQ concentration and WHO2005-TEQ concentration at different heating temperatures were listed in Table 3. With respect to total concentration reduction rates, 98.8%, 99.2% and 99.3% of total reduction rates were gained at 300 °C, 350 °C and 400 °C respectively. It was found that high chlorinated PCDD/Fs were favor of destruction than low chlorinated PCDD/Fs at all given temperatures, which suggests that the dechlorination reaction also takes place during the main destruction reaction process. However, the reduction rates of I-TEQ concentration was favored at 350 °C, the increase of O₈CDD at 400 °C decreased the total I-TEQ reduction rates. The difference between WHO2005-TEQ and I-TEQ was mainly due to the difference of TEQ factors of 1, 2, 3, 7, 8-P₅CDD,

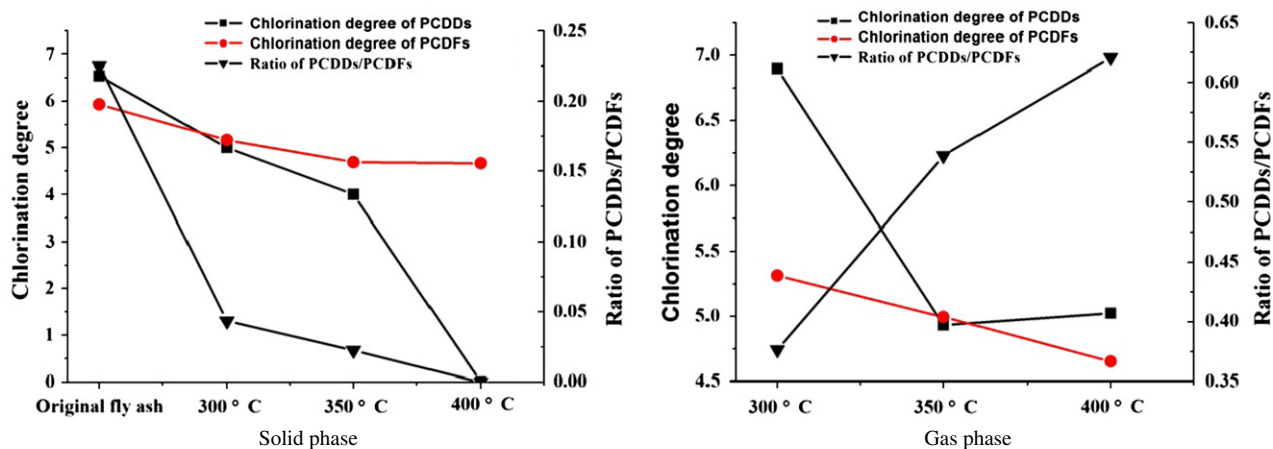


Fig. 1. Characteristic of PCDD/Fs at different heating temperatures.

Table 3

Total reduction rates of PCDD/Fs congeners at different heating temperatures (%).

Congeners	Concentration			I-TEQ concentration			WHO2005-TEQ concentration		
	300 °C	350 °C	400 °C	300 °C	350 °C	400 °C	300 °C	350 °C	400 °C
T ₄ CDD	99.6	93.1	94.3	100	100	100	100	100	100
P ₅ CDD	98.6	98.5	98.3	100	100	100	100	100	100
H ₆ CDD	99.9	99.8	99.9	100	100	100	100	100	100
H ₇ CDD	99.8	100	100	99.6	100	100	99.6	100	100
O ₈ CDD	99.6	99.5	99.5	99.3	99.3	98.9	99.2	99.2	98.8
T ₄ CDF	95.4	96.9	97.2	100	90.3	96.9	100	90.3	96.9
P ₅ CDF	99.1	99.5	99.2	100	99.8	99.1	100	99.8	99.1
H ₆ CDF	99.3	99.6	99.8	97.8	99.4	99.6	97.8	99.4	99.6
H ₇ CDF	98.8	99.7	99.8	97.6	99.6	99.7	97.6	99.6	99.7
O ₈ CDF	100	100	100	100	100	100	100	100	100
Total PCDD/Fs	98.8	99.2	99.3	99.3	99.6	99.3	99.3	99.6	99.3

O₈CDD and O₈CDF, however, nothing different between them was seen, except a minor difference in OCDD. The total reduction rates of I-TEQ and WHO2005-TEQ were also the same. The high reduction rates of PCDD/Fs obtained from the experiment demonstrated that thermal treatment is possible a promising method for final treatment of fly ash which contains high level of PCDD/Fs, however, the composition of fly ash is also a key parameter, which might influence or dominate destruction efficiency of PCDD/Fs (Lundin and Marklund, 2005).

3.2. Flow rate influenced removal of PCDD/Fs in fly ash

The flow rate parameter was also tested in this study. Historically, researchers always paid attention to the influence of temperature and residence time on de novo formation of PCDD/Fs in fly ash, and to studies of formation/destruction by thermal treatment. Inert gas such as nitrogen gas and static condition were conducted when fly ash was treated, but just as carrier gas, relatively few experiments were conducted. In this study three different flow rates were conducted to find out the effect of flow rate on the dechlorination or destruction of PCDD/Fs in fly ash during thermal treatment and how they acted.

Table 4 shows that under thermal treatment with different flow rates, concentration of PCDD/Fs in fly ash showed large differences, at a flow rate of 2 cm s⁻¹, the concentration and I-TEQ concentration of PCDD/Fs dropped dramatically, from 836 000 ng kg⁻¹ and 19 000 ng I-TEQ kg⁻¹ in the original fly ash to 2490 ng kg⁻¹ and 50.2 ng I-TEQ kg⁻¹ respectively after it was treated, however, no difference between I-TEQ and WHO2005-TEQ was seen even at all given flow rates situation. With the increase of flow rate, the

total concentration of PCDD/Fs and congeners in the fly ash decreased correspondingly, however, a few T₄CDD and H₆CDD were detected at the flow rates of 4 cm s⁻¹, which might be due to analysis error, in case that no PCDD congeners were detected at the flow rate of 3 cm s⁻¹. PCDD congeners were more susceptible to be removed from fly ash even at the flow rate of 2 cm s⁻¹, whereas PCDF isomers were more stable. When the flow rate was increased, the total concentration of PCDD/Fs and I-TEQ were then decreased to 678 ng kg⁻¹ and 21.6 ng I-TEQ kg⁻¹ respectively at 3 cm s⁻¹, and then decreased to 393 ng kg⁻¹ and 12.8 ng I-TEQ kg⁻¹ respectively at 4 cm s⁻¹.

The PCDD/Fs in desorbed flue gas did behave different (Table 4), when the flow rate was at 2 cm s⁻¹, the total concentration of PCDD/Fs and I-TEQ was as low as 3830 ng kg⁻¹ and 22.7 ng I-TEQ kg⁻¹ respectively; and when the flow rate was elevated to 3 cm s⁻¹, the total concentration of PCDD/Fs and I-TEQ dropped to 2100 ng kg⁻¹ and 20.8 ng I-TEQ kg⁻¹ respectively. However, when the flow rate was elevated to 4 cm s⁻¹, the total concentration of PCDD/Fs and I-TEQ increased dramatically to 37 000 ng kg⁻¹ and 824 ng I-TEQ kg⁻¹ respectively. It was found that the huge increase of PCDD/Fs was mainly due to the increase of PCDF especially higher chlorinated PCDFs such as H₇CDF, whereas no increase or a bit increase of PCDDs was detected at 4 cm s⁻¹. Addink and Olie (1995) pointed out that under nitrogen gas no PCDD/Fs was formed in fly ash, however, under static condition PCDD/Fs formation could be seen, the reason for which was ascribed to the O₂ diffusion into the fly ash bed because their experimental system was not sealed, rather from O₂ already present in the fly ash. Stieglitz et al. (1991) also found that under O₂ condition increased flow rate from 50 mL min⁻¹ to 250 mL min⁻¹ a trend to

Table 4
Concentration of PCDD/Fs congeners at different flow rates (ng kg⁻¹).

Congeners	2 cm s ⁻¹		3 cm s ⁻¹		4 cm s ⁻¹	
	Solid phase	Gas phase	Solid phase	Gas phase	Solid phase	Gas phase
T ₄ CDD	54.8	688	ND	ND	16.4	37.9
P ₅ CDD	ND	418	ND	59.7	ND	ND
H ₆ CDD	ND	49.4	ND	14.2	2.80	63.2
H ₇ CDD	ND	ND	ND	145	ND	ND
O ₈ CDD	ND	182	ND	140	ND	ND
Total PCDDs	54.8	1340	ND	359	19.2	101
T ₄ CDF	1560	1240	332	1020	190	1480
P ₅ CDF	294	414	59.8	355	51.6	2510
H ₆ CDF	350	440	156	249	40.4	7630
H ₇ CDF	231	392	131	117	92.2	25 300
O ₈ CDF	ND	ND	ND	ND	ND	ND
Total PCDFs	2435	2490	678	1740	374	36 900
Total PCDD/Fs	2490	3830	678	2100	393	37 000
I-TEQ	50.2	22.7	21.6	20.8	12.8	824
WHO2005-TEQ	50.2	22.6	21.5	20.7	12.8	824

concentrations higher by 30% to 60% was detected. In this study the whole system was sealed so O₂ could not react when flow rate was elevated to 4 cm s⁻¹ and no formation reaction could take place. The raise of PCDFs in the gas phase at the flow rates of 4 cm s⁻¹ might be due to the high vapor pressure of PCDFs, and it is easy to evaporate from fly ash at higher flow rates, so the dechlorination and destruction reactions could be reduced.

Chlorination degree of PCDD/Fs demonstrates the dechlorination process of PCDD/Fs during thermal treatment (Fig. 2). It could be found that in the solid phase of fly ash, chlorination degree of PCDD/Fs stood still or changed little. the chlorination degree of PCDDs at flow rate of 3 cm s⁻¹ dropped to zero, indicating that no detectable PCDDs were analyzed. However, only tetra- to octachlorinated PCDD/Fs was measured in this experiment, so the chlorination degree of zero was equal to four. In the gas phase of flue gas, the chlorination degree of PCDDs still changed little, even a significant decrease at flow rate of 4 cm s⁻¹, indicating that the dechlorination reaction still existed. However, huge increase of chlorination degree of PCDFs at 4 cm s⁻¹ was seen after a slight decrease of chlorination degree at 3 cm s⁻¹, the raise of chlorination degree was mainly due to the increase of P₅CDF, H₆CDF and H₇CDF. The result suggests that higher flow rate of inert gas could not reduce the total removal efficiency of PCDDs, but in deed could reduce dechlorination and followed destruction reaction of PCDFs on the surface of fly ash, which could then be desorbed to flue gas. However, further research on the mechanism of this phenom-

enon has not been studied. The change of the ratio of PCDDs/PCDFs in fly ash was little, and the ratios of PCDDs/PCDFs at all flow rates experiment were small, which was due to the high removal efficiency of PCDDs; the decrease of PCDDs/PCDFs in the flue gas was due to fast dechlorination and destruction reaction of PCDDs at 3 cm s⁻¹, and at 4 cm s⁻¹, the decrease of PCDDs/PCDFs was mainly contributed to high emission of PCDFs to the gas phase.

The total concentration reduction rates of PCDD/Fs at flow rates of 2, 3 and 4 cm s⁻¹ were 99.2%, 99.7% and 95.6% respectively (Table 5). The reduction rates of total concentration and congeners increased when the experimental condition of flow rate was increased from 2 cm s⁻¹ to 3 cm s⁻¹. However, when the flow rate was set at 4 cm s⁻¹, the reduction rate decreased significantly, which was mainly contributed to large decrease of P₅CDF, H₆CDF and H₇CDF as former mentioned, especially for H₇CDF, reduction rate of only 86.2% was achieved, which might be due to the reason that high flow rate reduces the dechlorination and destruction reactions of higher chlorinated PCDFs on the surface of fly ash, then the PCDFs could be desorbed from fly ash; nevertheless, PCDDs are much more stable in chemical characteristic than PCDFs (Lundin and Marklund, 2008), so could not easily be desorbed from fly ash, and consequently PCDDs are susceptible to dechlorination than the PCDFs at relative low temperatures (Addink et al., 1995b). It was similar with the trend of I-TEQ, the reduction rates were 99.6%, 99.8% and 95.6% at the flow rates of 2, 3 and 4 cm s⁻¹ respectively, and the main contributors of reduction rate

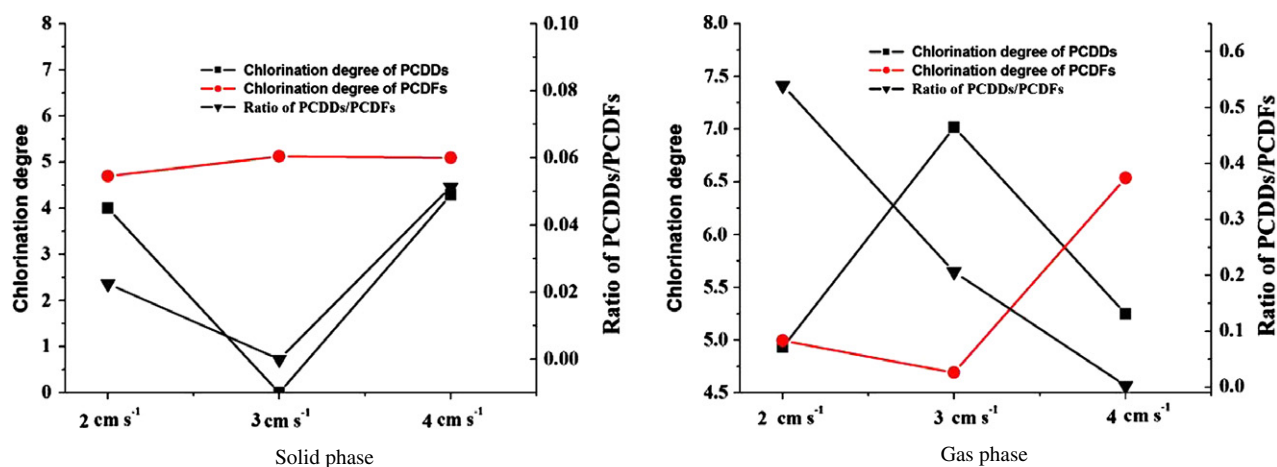


Fig. 2. Characteristic of PCDD/Fs at different flow rates.

Table 5
Total reduction rates of PCDD/Fs congeners at different flow rates (%).

Congeners	Concentration			I-TEQ concentration			WHO2005-TEQ concentration		
	2 cm s ⁻¹	3 cm s ⁻¹	4 cm s ⁻¹	2 cm s ⁻¹	3 cm s ⁻¹	4 cm s ⁻¹	2 cm s ⁻¹	3 cm s ⁻¹	4 cm s ⁻¹
T ₄ CDD	93.1	100	99.5	100	100	100	100	100	100
P ₅ CDD	98.5	99.8	100	100	100	100	100	100	100
H ₆ CDD	99.8	99.9	99.7	100	100	100	100	100	100
H ₇ CDD	100	99.7	100	100	99.6	100	100	99.6	100
O ₈ CDD	99.5	99.6	100	99.3	99.4	100	99.2	99.4	100
T ₄ CDF	96.9	98.5	98.1	90.3	100	100	90.3	100	100
P ₅ CDF	99.5	99.7	98.3	99.8	99.7	96.6	99.8	99.7	96.6
H ₆ CDF	99.6	99.8	96.3	99.4	99.8	93.8	99.4	99.8	93.8
H ₇ CDF	99.7	99.9	86.2	99.6	99.7	83.8	99.6	99.7	83.8
O ₈ CDF	100	100	100	100	100	100	100	100	100
Total PCDD/Fs	99.2	99.7	95.5	99.6	99.8	95.6	99.6	99.8	95.7

decreasing at flow rate of 4 cm s⁻¹ were also P₅CDF, H₆CDF and H₇CDF. No apparent difference of reduction rates between I-TEQ and WHO2005-TEQ was seen.

4. Conclusions

The characteristics of medical waste incinerator fly ash are different from those of municipal solid waste incinerator fly ash because wastes components such as plastics and paper are different. Fly ashes also differ due to the incineration conditions and APCDs and maybe due to the different composition of the waste, and in most cases exceed in PCDD/Fs, PCBs and other POPs. Thermal treatment of such kind of fly ash under inert gas is promising if landfill is strictly controlled. PCDD/Fs in fly ash can be largely removed under suitable heating temperature and carrier gas flow rate, and dechlorination and destruction reactions take important part in the removal of PCDD/Fs; in the flue gas, PCDD/Fs could be rarely be desorbed, which may be mainly due to the physicochemical characteristics of PCDD/Fs. However, the composition of fly ash is also a key parameter which may influence or dominate destruction efficiency of PCDD/Fs. The most interesting and remarkable result demonstrates that when flow rate is higher than 4 cm s⁻¹, destruction efficiency of PCDD/Fs decreases dramatically, and the main contributors are P₅CDF, H₆CDF and H₇CDF desorbed to flue gas. It has not been reported ever since, and indicates that we must take flow rate into consideration when pilot or large-scale thermal treatment furnace is operated in order to eliminate concentration of PCDD/Fs in fly ash, and series of following work should be done to study the mechanism how PCDD/Fs desorbs from fly ash and be decreased in destruction efficiency.

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