Review

Comparative evaluation of techniques for controlling the formation and emission of chlorinated dioxins/furans in municipal waste incineration

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Abstract

Chlorinated dioxins and furans are highly toxic micropollutants emitted from combustion sources, in particular, municipal solid waste incinerators. Because of concerns over their adverse health effects, a number of countries have introduced stringent emission limits for chlorinated dioxins and furans. The technologies for reducing their formation and emission in incineration processes have been studied extensively. In this paper, the state of the art in this technical field is reviewed including techniques for (i) removal of PCDD/Fs in flue gases; (ii) treatment of fly ash for destruction of PCDD/Fs; (iii) prevention of PCDD/F formation in the postcombustion zone of incinerators; (iv) combustion measures to reduce PCDD/F formation; and (v) control of waste composition and properties. For these techniques, comparative data are given, the theories are discussed and recommendations are made. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The formation and emission of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) from municipal solid waste incinerators (MSWI) have been a subject of extensive research in the past 20 years, because of serious concerns over the adverse

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health effects of PCDD/F in the environment. In particular, around 1990 several European countries that have large municipal solid waste incineration capacities have issued stringent emission limits of 0.1 ng-TE/Nm^3 for PCDD/F. The technologies to achieve this goal in an industrial scale are needed and have been under active development. The current status of PCDD/F emission control in Germany has been reviewed by Johnke and Stelzner [1], and also by Lahl et al. [2]; the situation in the Netherlands has been reviewed by Born [3], while the development in Japan has been given by Hiraoka and Okajima [4]. In the papers by Acharya et al. [5], Reimann [6] and Kilgroe [7], useful discussions about the techniques for PCDD/F emission control have been presented.

A great deal of the previous work is, however, concerned mainly with the removal of PCDD/F from flue gases by end-of-pipe measures such as wet/dry scrubbing, fabric filtration, active carbon injection, etc. The techniques for controlling PCDD/F formation in the incineration processes seem to have not yet been fully explored. In this article, we will review the PCDD/F formation and emission control technologies with an emphasis on the possible techniques for preventing PCDD/F formation in the postcombustion zone of incinerators. Table 1 provides a framework for the discussion and also shows the structure of this article. For each technique in Table 1, comparative data will be given, the theories will be discussed and recommendations be made. The formation mechanism of PCDD/F in combustion processes has already been dealt with in many papers, e.g. Refs. [8–11], and thus is not discussed here; the readers are referred to these published papers for the necessary background about the mechanism of PCDD/F formation.

2. Removal of PCDD/Fs in flue gases

2.1. Background

As an end-of-pipe technique, the removal of PCDD/Fs in flue gases is necessary to reduce the emissions of PCDD/Fs to the environment. A number of equipments have been tested such as ESP, scrubber, bag filter, adsorbent injection, and a combination of these under different operating conditions. The combination of a scrubber, a bag filter coupled with activated carbon injection has been found to be a most effective technique for PCDD/F emission control. Another promising technique is the catalytic decomposition using oxidation or reduction catalysts.

2.2. Scrubber and bag filter coupled with active carbon adsorption

According to the method of active carbon addition, three kinds of processes can be found: the entrained-flow, moving-bed and fixed-bed process. In the entrained-flow process, active carbon is injected before the bag filter and carried by the flue gas to the filter where it builds up a carbon layer which removes PCDD/F from the flowing gas; the spent active carbon is cleaned off the bag together with other particulate matter at certain time intervals. In the moving-bed process, flue gases are passed through a

Table 1
Overview of possible techniques for controlling the formation and emission of PCDD/Fs in municipal waste incineration

Measures	Technologies
Removal of PCDD/F in flue gas	Dry/semidry/wet scrubber and bag filter coupled with activated carbon adsorption (entrained-flow, moving-bed or fixed-bed processes)
	Catalytic decomposition
	Chemical treatment
Treatment of fly ash for destruction of PCDD/F	Thermal treatment
	Catalytic treatment
	UV irradiation
	Chemical reagent
	Hydrothermal treatment
	Ultrasonic treatment
Prevention of PCDD/F formation in the postcombustion zone	Control of the temperature-time profile of flue gases
	High-temperature separation of fly ashes (multiple cyclones, high-temperature ceramic filters)
	Boiler design and soot blowing
	Injection of inorganic additives (SO_2, SO_3, NH_3, CaO, $CaCO_3$, $Ca(OH)_2$, $Mg(OH)_2$, H_2O_2, O_3, HNO_2, HNO_3, $(NH_4)_2Fe(SO_4)_2$, etc.)
	PCDD/F formation inhibitors (2-aminoethanol, urea, triethanolamine, ethan-1,2-diol, 3-aminopropanol, ammonia sulfide, ethylenediaminetetraacetic acid, nitrilotriacetic acid, etc.)
Improvement of combustion conditions	Optimization of combustion parameters (O_2, excess air ratio, secondary/primary air ratio, temperature, H_2O, CO, etc.)
	Advanced combustor design
	Automatic combustion control systems
	Additives injection
Control of waste composition and properties	Separation of PVC
	Refuse derived fuels
	Additives

moving bed of active carbons, the fresh carbons are fed to the top of the bed and the spent carbons discharged from the bottom of the bed continuously or at certain time intervals. In the fixed-bed process, flue gases are passed through a fixed bed of active carbons, and the whole bed is replaced after certain service time. In all cases, the PCDD/F are removed from flue gases by adsorption on the carbon.

Some performance data of the various processes are given in Table 2. It can be seen that: (1) The PCDD/F removal efficiencies are typically $> 95\%$ and the PCDD/F concentrations in the treated gases are below the 0.1 ng-TE/Nm^3 emission limit by a large margin. (2) Active carbon consumption is about 50 mg/Nm^3 in entrained-flow processes. In moving- or fixed-beds, the active carbon consumption is relatively low. (3) Many studies have shown that the operating temperature of bag filters is an important factor affecting the PCDD/F collection efficiencies and should be below 200°C, preferably between 120–150°C. (4) The disposal of carbon residues from the filters is in some cases by burning in the incinerator. These carbon residues contain PCDD/F and heavy metals (Hg in particular). The PCDD/F will be destroyed in the incinerator, but Hg will be recycled to the flue gas stream and largely removed by the scrubber. Filter cakes are sometimes combined with bottom and boiler ashes and are disposed of in landfills.

2.3. Catalytic decomposition

Selective catalytic reduction (SCR) units are commonly used in coal-fired power plants for controlling NO$_x$ emissions. In some MSWI plants, SCR units have also been installed. In the late 1980s, it was found out incidentally that SCR also decomposes PCDD/Fs; Table 3 gives a summary of the relevant data. Commercial SCR catalyst is mostly composed of the oxides of Ti, V and W and is often used at a temperature range 300–400°C. In power plants, three installation positions for SCR units are possible: high dust (between boiler and ESP), low dust (between ESP and air heater) and tail-end. In MSWIs, SCR can only be installed at the tail-end after scrubber and bag filter because the heavy metals in the high and low dust positions rapidly decrease the catalytic activity of SCR units. The temperature of flue gases after bag filter is, however, typically below 150°C; at such low temperatures the performance of SCR in decomposing PCDD/Fs is not reliable. In Table 3, it can be seen that between 200 and 250°C additional PCDD/Fs are formed over some types of SCR catalysts. Consequently, reheating of the flue gas to 300°C is required if SCR is placed at the tail-end; this represents a considerable energy loss for MSWI operation. In recent research, catalysts that can decompose PCDD/Fs at about 200°C are sought, and it has been claimed by Sakurai et al. [17] that Pt and Au supported on silica–boria–alumina composite oxide are effective for PCDD/F decomposition at low temperatures. Industrial scale testing to verify this is required.

2.4. Some novel methods for treatment of flue gases to remove or destroy PCDD/Fs

The entrained-flow process using active carbon to remove PCDD/F consumes a large quantity of active carbon annually. In principle, for such a separation operation by

Table 2
Removal of PCDD/Fs from flue gases by the combination of scrubber, bag filter and activated carbon adsorption

Processes	Equipment	Performance data	Ref.
Entrained-flow	Wet scrubber, bag filter with AC injection (Trade name of AC: Sorbalit)	PCDD/F in (a) untreated gas: 2.17 ng-TE/Nm^3, (b) purified gas: 0.069 ng-TE/Nm^3. Removal: 96.8%	[12]
	Fabric filter ($T = 120°C$) with AC injection (90% of the AC residues from the filter are recirculated to the injection point)	AC dosage: 50 mg/Nm^3. PCDD/F (a) before filter: 0.24 ng-TE/Nm^3, (b) after filter: 0.01 ng-TE/Nm^3. Removal: 95.8%	[13]
Moving-bed	WKV/Integral counter-current activated coke process (flue gas inlet temperature: 120–165°C)	AC consumption: 500 t/yr/plant (total gas flow: 464 000 Nm^3/h). PCDD/F stack emission: 0.015 ng-TE/Nm^3	[14]
	Moving bed adsorber (flue gas inlet temperature: 150°C; space velocity: 1000/h)	AC consumption: 5 mm of bed height/day. PCDD/F in (a) feed gas: 100 ng/Nm^3, (b) treated gas: 1.2 ng/Nm^3. Removal: 98.8%	[15]
Fixed-bed	MEDISORBON/KOMBISORBON adsorber (a mixture of zeolite, carbon and inert material; flue gas inlet temperature: 40–100°C)	AC consumption: The whole bed is replaced after a few years. PCDD/F in (a) raw gas: 0.3 ng-TE/Nm^3, (b) clean gas: 0.05 ng-TE/Nm^3. Removal: 83% (After 23 100 h test duration)	[16]

AC = activated carbon.

Table 3
Decomposition of PCDD/Fs in flue gases by SCR units

Catalyst	Reactor Temperature (°C)	Space velocity (per h)	NH_3/NO_x molar ratio	PCDD/F in flue gas (ng-TE/Nm^3)			Ref.
				Inlet	Outlet	Removal (%)	
Pt and Au on silica–boria–alumina composite oxide	220	3000	0	0.25	0.01	96	[17]
V_2O_5–WO_3–TiO_2	250	3000	0	0.35	1.6	Increase	[17]
Pt on V_2O_5–WO_3–TiO_2	250	3000	0	0.15	0.63	Increase	[17]
			0.8	0.09	0.1	Increase	
SCR DeNO$_x$	300	n.a.	with NH_3	2.2	0.84	61.8	[18]
SCR DeNO$_x$	200	n.a	with NH_3	0.34	0.05	85.3	[19]
SCR DeNO$_x$	200	n.a.	n.a.	0.01	0.11	Increase	[20]
	230	n.a.	n.a.	0.39	0.02	94.9	
V_2O_5–WO_3–TiO_2	280	n.a.	n.a.	1.64	0.05	97	[21]
SCR DeNO$_x$	325	n.a.	with NH_3	0.05	0.01	80	[22]
Pt supported	300–400	20 000	0	90[b]	30[b]	66.7	[23]

n.a. = Not available.
[a] Area velocity $(Nm^3/m^2/h)$.
[b] In ng-PCDD/Nm^3.

adsorption, it is possible to use a system of one adsorber and one regenerator, i.e. two identical vessels containing a fixed-bed or fluidized-bed of active carbons, and these two vessels are used alternatively; while one performs adsorption to remove PCDD/Fs from flue gases, another is passed by fresh air to desorb PCDD/Fs and regenerate the active carbons. However, in PCDD/F separation, the PCDD/F molecules are believed to be strongly adsorbed or deeply entraped in the microporous structure of the carbons so that desorption of PCDD/F is very difficult. In the DIOXIN'95 Symposium, Kreisz et al. [24] proposed that technical plastics may be used for PCDD/F adsorption at temperatures between 60–80°C, and PCDD/F desorption may be performed at 130°C, thus a system using one adsorber and one regenerator to continuously remove PCDD/Fs from flue gases without producing carbon residues is feasible.

Some methods for chemical treatment of flue gases to destroy PCDD/Fs have also been proposed. For example, Siret et al. [25] and Vicard [26] reported a two-stage wet scrubbing process where in the first-stage lime is injected to remove acidic gases, and in the second-stage soda, carbon and proprietary additives are injected to destroy PCDD/Fs. The system removes more than 98% of PCDD/Fs in the raw gas, and destroyed about 84% of the PCDD/Fs accounting for all the effluent streams in the system.

2.5. Discussion

The current technology for removal of PCDD/Fs from flue gases relies heavily on active carbon injection and fabric filtration. The advantages of this practice are that: (1) it can conveniently be carried out and retrofitting of existing plants is relatively easy; and (2) the emission limit of 0.1 ng-TE/Nm^3 can be reached with a large safe margin when the process parameters such as the temperature of bag filters and the active carbon injection are optimized. The disadvantages of this practice are that: (1) the pollutants are merely transferred from air to solid residue and to land; (2) the active carbon consumption increases the cost of waste incineration considerably; and (3) more space and capital investment are required to install the scrubber and bag house. An alternative is to use a moving-bed or fixed-bed carbon adsorber behind the filter. This method may decrease the carbon consumption and lower the operating cost; but the fire hazard and service lifetime of the adsorber are still problematic. Decomposition of PCDD/Fs in flue gases using a fixed bed of SCR catalysts placed after the filter has not yet proved successful in the operating temperature range around 200°C. Other novel processes such as the carbon adsorber–regenerator system and chemical treatment also require more studies.

3. Treatment of fly ash for destruction of PCDD/Fs

3.1. Background

The solid residues from MSW incineration contain dioxins and heavy metals. Typically, filter cake from MSW incineration has a dioxin content of 6 ng-TE/g, ESP ash has 4 ng-TE/g, boiler ash has 0.2 ng-TE/g, bottom ash has 0.03 ng-TE/g while municipal solid waste has 0.09 ng-TE/g [10]. In some countries, the environmental

protection legistration classifies MSWI fly ash as hazardous material and further treatment is required before they can be disposed of in landfills.

3.2. Thermal treatment

Vogg and Stieglitz [27] and Stieglitz and Vogg [28] have demonstrated that PCDD/F present in fly ash can be decomposed by thermal treatment under suitable conditions. Their work revealed that: (1) in an oxidative atmosphere, thermal treatment at 600°C for 2 h resulted in ca. 95% decomposition of PCDD/F, but at lower temperatures PCDD/F are formed; and (2) in an inert atmosphere, thermal treatment at 300°C for 2 h resulted in ca. 90% decomposition of PCDD/F. These findings are the basis of some industrial processes for thermal decomposition of PCDD/F listed in Table 4. Notice in particular the relationship between treatment temperature, time and atmosphere; under an inert atmosphere low-temperature treatment may be used, but under an oxidative atmosphere high-temperature treatment is required; and at temperatures higher than 1000°C the processing time for PCDD/F decomposition is relatively short. All the industrial processes listed in Table 4 were reported to be able to obtain more than 95% destruction of PCDD/Fs.

Table 4 also lists the PCDD/F concentrations in the exhaust gas from the fly ash treatment processes. According to current theory of PCDD/F formation, the combination of flue gas and dust containing residual carbon, heavy metal and chlorine under suitable conditions will generate PCDD/F. In the PCDD/F decomposition equipments listed in Table 4, there is always a transit temperature zone of 200–500°C for the exhaust gas and dust as well as for the treated fly ash. So there is the possibility that PCDD/F are reformed in the low-temperature region of these PCDD/F decomposition equipments when the exhaust gas and fly ash are cooled down. Data given in a paper by Abe et al. [33] show that downstream of a fly ash melting furnace, the flue gas PCDD/F concentration in the inlet of a gas cooler is 0.13 ng-TE/Nm^3 and in the outlet of the gas cooler is 0.54 ng-TE/Nm^3; the flue gas PCDD/F concentration has increased by a factor of 4 in the gas cooler probably due to the de novo synthesis. Data given in another paper by Takasuka et al. [35] show that fly ash after thermal treatment in a rotary kiln can regenerate PCDD/F when kept at 300°C for 2 h. Thus in these PCDD/F decomposition equipments regeneration of PCDD/F in the postfurnace zone of the equipments seems to be occurring in some instances and it is necessary to take measures to rapidly cool down the treated ash and the exhaust gas to prevent PCDD/F regeneration. APCDs such as scrubber and bag filter should also be installed to control PCDD/F emissions.

3.3. Other treatment methods

A number of other treatment methods for destruction of PCDD/F in fly ash has been reported in the literature. The base catalyzed decomposition (BCD) process is a chemical treatment process for decomposing PCBs; this process has also been tested for decomposing PCDD/F recently [39,40]. In a BCD process, solid or liquid wastes comtami-

Table 4
Thermal treatment of fly ash for decomposition of PCDD/Fs

Equipment	Reactor temperature (°C)	Time	Atmosphere	PCDD/F concentration				Ref.
				Untreated ash (ng-TE/g)	Treated ash (ng-TE/g)	Comb. gas[a] (ng-TE/Nm^3)	Destruction (%)	
Lab furnace	600	2 h	Air	753[b]	27[b]	Detected	96.4	[27]
Lab furnace	300	2 h	N$_2$	296[b]	25[b]	n.a.	91.6	[28]
Lab oven	300	2 h	N$_2$	235[b]	30[b]	n.a.	87.2	[29]
Electrical heated reactor (500 kg-ash/h)	350	1 h	N$_2$	0.6	0.002	Detected	99.7	[19]
Electrical heated reactor (30–80 kg-ash/h)	415	1.2 h	N$_2$	3.5	0.019	0.002	99.5[c]	[30]
Lab chamber oven	1500	10 min	Air	2.4	0.0003	n.a.	99.98	[31]
Coke-bed melting furnace (30 kg-ash/h)	1300	8 min	Comb. gas	7.3	0.001	23	97[c]	[32]
Oil burning melting furnace (18.5 t-ash/day)	1300	n.a.	Comb. gas	10	0.00	0.54	99.98[c]	[33]
Sintering in LPG burning furnace (10 kg-ash/bench)	1000	50 min	Comb. gas	2.8	0.00	8.3	96.4	[34]
Rotary kiln with electric heater (18 kg-ash/h)	500	4.5 min	Air or N$_2$	1.9	0.09	n.a.	95.3	[35]
Plasma melting furnace (300 kg-ash/h)	1380	n.a.	Comb. gas	2.3	< 0.01	Detected	98.4	[36]
Heat treatment at the bottom of boiler section in MSWI	n.a.	30 min	MSWI Flue gas	1	0.01	n.a.	99	[37]
Butane gas burning swirling-flow melting furnace (100 kg-ash/h)	1300	n.a.	Comb. gas	2.8	0.0012	1.8	98.9	[38]

[a] The exhaust gas resulting from the thermal treatment of fly ash.
[b] In ng/g.
[c] Based on PCDD/F flow balance of all effluent streams of the process including gas, slag, dust, drain, etc.

nated by chlorinated organic compounds are mixed with paraffin oil, sodium hydroxide and carbonaceous catalyst, and heated at 300–350°C for several hours. The paraffin oil provides hydrogen needed for the dechlorination of chlorinated organic compounds; then the chlorine is neutralized by sodium hydroxide into sodium chloride. The BCD process has been reported to be very effective for the decomposition of PCDD/F. Another chemical treatment process utilizes the scrubber-phase hydrogenation at 270–450°C over a fixed-bed of Pd-on-spinel catalyst to destroy chlorinated organic compounds [41].

The hydrothermal decomposition of PCDD/F and other halogenated hydrocarbons has been studied by some investigators [42,43]. Fly ash was put into water or a solution and subject to hydrothermal treatment at high pressure and temperature. An effective solution for PCDD/F decomposition was found to be NaOH containing methanol; fly ash containing 1100 ng/g total PCDD/F subjected to hydrothermal treatment using this solution at 300°C for 20 min was found to have only 0.45 ng/g total PCDD/F. It was suggested that the process is superior to purely thermal treatment at the same temperature.

3.4. Discussion

Thermal destruction of PCDD/F in fly ash has been widely studied and has gained some industrial applications. A potential problem is that when the heat source is provided by electric heating, the electricity consumption could be costly; but when the heat source is provided by burning fuels such as coke, oil or gas and the fly ash is in contact with the combustion gas, there is the possibility of PCDD/F regeneration in the low-temperature zone of these PCDD/F decomposition equipments. Also more APCDs are needed to clean up the exhaust gases. Other methods such as the chemical and hydrothermal treatment are in a laboratory testing stage. In view of the high acid and heavy metal load in MSWI flue gases it is desirable to operate some integrated process that can simultaneously recover the acid and heavy metals and destroy the PCDD/Fs. For example, in the 3R process the heavy metal recoveries of about 90% for Cd, 65% for Zn and 20% for Pb and Cu were achieved, and the PCDD/Fs in fly ash were decomposed according to a pilot scale plant study [44].

4. Prevention of PCDD/F formation in the postcombustion zone of incinerators

4.1. Background

As discussed in Sections 2 and 3 the current technology for PCDD/F emission control relies on removal of PCDD/F from flue gases which significantly increases the construction and operation costs of MSWIs. And the solid residues from flue gas cleanup are difficult to handle. Therefore, it is very much desirable to prevent PCDD/F formation in the combustion processes at the first place. How to prevent PCDD/F

formation in combustion has already been studied for a number of years; this section will discuss the proposed techniques and available experimental data so far.

4.2. Control of the temperature–time profile of flue gases

It has been well demonstrated that PCDD/F are formed in the postcombustion zone of incinerators; the critical temperature range for PCDD/F formation is between 200 and 500°C with maximum formation rate at about 300°C. Therefore, if the flue gas residence time in this temperature range is shortened, the amount of PCDD/F formed is likely to be decreased. Thus a possible technique for suppressing PCDD/F formation is by rapid cooling of the flue gases. This idea has been suggested by many researchers in the past.

Some experimental data verifying this technique can be found in the literature. For example, Fangmark et al. [45–47] have studied PCDD/F formation in a laboratory-scale fluidized-bed combustor. The flue gases from the combustor were passed though some pipes; and by cooling, electric heating or adjusting the insulation on these pipes the influence of flue gas temperature profile on PCDD/F formation was studied. Their work suggested that flue gas temperature profile is the most important factor in PCDD/F formation and the flue gas should be rapidly cooled to below 260°C to suppress PCDD/F formation. Ghorishi and Altwicker [48] studied the influence of postcombustion temperature on PCDD/F in a spouted-bed combustor. They found that when the postcombustion zone was held nearly isothermal (inlet: 430°C, outlet: 390°C), the PCDD/F concentration measured at the outlet of the postcombustion zone was 122.5 ng/Nm^3; when the same postcombustion zone was quenched (inlet: 430°C, outlet 125°C), the PCDD/F concentration at outlet was decreased to 30.9 ng/Nm^3. Vogg et al. [49] connected two small flue gas bypass lines to a boiler of an incinerator; one bypass line was provided with a water cooling section, and the other with a water quenching reactor. The PCDD/F concentration at the outlet of the bypass line with water quenching was found to be about half of that with cooling. Watanabe et al. [50] compared PCDD/F formation in a mainline and a branch line connected to a fluidized-bed incinerator. The branch line boiler has a shorter flue gas residence time and less dust deposition than the mainline boiler, and was found to have less PCDD/F formation compared with the mainline. In a patent specification Hiltunen et al. [51] reported that PCDD/F formation is reduced when flue gases are cooled rapidly in a circulating fluidized-bed at a cooling rate as high as 1000°C/s.

A key parameter in these experiments is probably the average flue gas cooling rate. Some data of the flue gas cooling rates estimated from the above experimental reports and the corresponding PCDD/F formation levels are listed in Table 5. The effect of cooling rates on PCDD/F formation is evident. In a waste heat boiler the flue gas cooling rates are usually in the range of 100–200°C/s, and the PCDD/F level at boiler outlet is typically 5 ng-TE/Nm^3. To achieve a PCDD/F level of 1 ng-TE/Nm^3 at boiler outlet, a cooling rate in the range of 500–1000°C/s is probably necessary. However, in practice such a high cooling rate is difficult to reach as the volume of flue gases is large. When using water quenching, the loss of the heat-recovery efficiency in MSWI is one of the factors that should be considered.

Table 5
Influence of flue gas cooling rates on PCDD/F formation

Test facility and the postcombustion region studied	Flue gas temperature[a] (°C)		Flue gas residence time (s)	Average flue gas cooling rate (°C/s)	PCDD/F concentration at outlet	Ref.
	Inlet	Outlet				
Lab fluidized-bed combustor followed	750	340	2.9	140	28 ng-TE/Nm^3	[46]
by flue gas pipes which are cooled,	750	260	2.9	170	6.5 ng TE/NM^3	
electrically heated or insulated to						
study the effects of temperature						
profile on PCDD/F						
Industrial-scale fluidized-bed incinerator	700	320	3.7	100	80^b	[50]
followed by a flue gas mainline and a branch	600	250	1.5	230	10^b	
line which has a boiler with short gas residence						
time and prevention of dust deposition						
Grate-type incinerator followed by a	830	400	n.a.	500–1000	140 ng/Nm^3	[51]
circulating fluidized-bed of sand	830	300	n.a.	500–1000	72 ng/Nm^3	
which cools down the flue gases						

[a] Of the postcombustion section studied.
[b] Boiler oulet/inlet.

4.3. High-temperature separation of fly ashes

The extensive laboratory simulation studies so far have shown that PCDD/F formation reactions are catalyzed by fly ash surfaces or certain metal components in the fly ash surfaces (Cu and Fe in particular). If the fly ashes can be separated out from the flue gases prior to the critical temperature region of 200–500°C, then PCDD/F formation should be decreased significantly. Thus high-temperature separation of fly ashes has long been considered to be effective in reducing PCDD/F formation though few experimental data in a plant scale are available to support this. Recently, Fangmark et al. [45–47,52] studied PCDD/F formation in postcombustion zone when (a) there is no fly ash separation in the entrance of the postcombustion zone; (b) there is fly ash separation using a cyclone; and (c) there is fly ash separation using a cyclone followed by a filter. Their experimental data are compiled in Table 6. It can be seen that in contrary to expectation, high-temperature separation of fly ashes has not reduced PCDD/F formation in this case; instead, it appears that when more fly ash collection equipments are added, more PCDD/F are formed. It may be noted that Table 6 includes only the PCDD/F concentrations in the flue gases; if the PCDD/F in cyclone ash and filter cake were also included, the total amount of PCDD/F generated when installing fly ash separation equipments would be much higher than those shown in Table 6. Another experiment studying the effect of flue gas dedusting on PCDD/F formation is that by Hunsinger et al. [53]. Here the flue gases from an incinerator were passed through some sampling trains consisted of a filter, a condensor and an adsorber; the filter temperature was varied and it was found that below 200°C the filter temperature had no influence on PCDD/F, but above 200°C more PCDD/F were formed when the filter temperature was increased. In another experimental setup a cyclone was added before the filter, but was found to have no effect on PCDD/F formation. In sum, it appears that the high-temperature separation of fly ash for PCDD/F formation control has not yet proved successful. A reason for this is probably that the condition at the fly ash collecting equipments are also susceptible for PCDD/F formation.

4.4. Boiler design and soot blowing

It has been suggested that residual carbon in fly ash is the main carbon source for de novo synthesis of PCDD/Fs. Fly ash deposited in the heat exchange surfaces of a waste heat boiler may have a residence time up to several hours or days and make a significant contribution to the observed PCDD/F levels in MSWI. Thus one might assume that if the fly ash in heat exchange surfaces are cleaned off regularly, then less PCDD/Fs will be formed. Usually industrial boilers are equipped with soot-blowers which use steam, compressed air or water jet to blow away ash deposits in order to reduce boiler fouling. Some data concerning the effect of soot-blowing on PCDD/F levels can be found. Jager et al. [54] reported that during soot-blowing the flue gas particulate load, PCDD/F load and the overall PCDD/F emissions were increased by 10-, 30- and three-folds, respectively, compared with normal operation. Johnke and Stelzner [1] also reported that when using soot-blowing, the dust content of raw gas, PCDD/F concentrations in raw

Table 6
Effect of high-temperature separation of fly ashes on PCDD/F formation (compiled from Refs. [45–47,52])

Postcombustion zone		Flue gas PCDD/F concentration at outlet of the postcombustion zone (ng-TE/Nm^3)		
Temperature (°C)	Residence time (s)	Without cyclone, without filter	With cyclone, without filter	With cyclone, with filter
260	0.9	0.23	4.5	17 or 210
260	1.4	2.9	19	87
260	2.9	6.5	24	11 or 20
340	0.9	5.6	3.3	170
340	1.4	4.9	8.6	170
340	2.9	28	17	6.9
430	0.9	2.7	3.6	10
430	2.9	3.3	4.1	66 or 54
510	0.9	3.5	7.9	160
510	1.4	6.3	8.3	220 or 120
340	1.4	2.2	4.4	34
340	1.4	3.5	14	92

gas and in clean gas were increased by 6-, 30- and three-folds, respectively. Hence it appears that soot-blowing increases PCDD/F emissions. Nonetheless, few data about the influence of soot-blowing frequency on overall PCDD/F formation level in the boiler section over a long operation period are available; probably, more frequent cleaning of the heat surfaces will lead to a lower PCDD/F formation level if all the gas and solid discharges are accounted for in the calculation.

4.5. Injection of inorganic additives

The studies of inorganic additives for reducing PCDD/F formation are reviewed in this section. Organic additives will be reviewed in Section 4.6.

4.5.1. Sulphur compounds

In 1986, Griffin [55] proposed that the high sulphur content of coal is the cause for the low PCDD/F emissions from coal combustion. This proposal has stimulated much research about the possiblity of adding sulphur compounds to incineration processes in order to reduce PCDD/F formation. A lot of experimental data are available, and Table 7 compiles some of them [56–64].

In laboratory simulation studies, either 'de novo synthesis' or 'precursor formation' experiment, SO_2 can be introduced into the gaseous reactant stream to investigate its effect on PCDD/F formation. When SO_2 was added, increasing PCDD/F formation [56,58], decreasing PCDD/F formation [57] and no significant effect [59] have all been observed. In pilot- or full-scale combustor studies when sulphur compounds were added, a reduction of PCDD/F emissions has been observed in many cases; but there are also other reports that PCDD/F reduction could not be observed. At present the technique of reducing PCDD/F emissions by sulphur compound addition has not been well developed or proved.

Sulphur compounds may be added in several ways: gaseous SO_2 or SO_3 injection into the combustion chamber or boiler section, or sulphur containing materials mixed with MSW fuels. It appears that for PCDD/F reduction the co-combustion of sulphur compounds with MSW is most effective, the injection of SO_2 in combustion zone less effective, and in boiler section least effective. But the effects are not always observable or controllable.

Theoretical considerations about the inhibitory effect of sulphur on PCDD/F formation have been given by several authors in the past. (1) The original proposal by Griffin [55] was based on thermodynamic calculation. In short, chlorination of aromatics by Cl_2 is more favourable than by HCl; Cl_2 may be generated in situ from HCl according to: $2HCl + 1/2O_2 \rightarrow Cl_2 + H_2O$; the presence of SO_2 and H_2O reduces Cl_2 through the reaction: $Cl_2 + SO_2 + H_2O \rightarrow SO_3 + 2HCl$; hence the formation of chlorinated aromatics (including PCDD/F) may be reduced. (2) Gullett and co-workers [59,60] proposed that the role of sulphur is to reduce the catalytic activity of fly ash by reacting with the metal components in fly ash through reactions such as: $CuO + SO_2 + 1/2O_2 \rightarrow CuSO_4$; since $CuSO_4$ is much less effective for PCDD/F synthesis than CuO. (3) Gullett et al. also proposed that the presence of SO_2 may sulfonate the phenolic PCDD and PCDF

Table 7
Effect of sulphur compound addition on PCDD/F levels[a]

Experiment	Mode and amount of sulphur compound addition	Flue gas SO_2 level	PCDD/F level	Change in PCDD/F	Ref.
Lab-scale de novo synthesis experiment (genuine fly ash passed by air at 300°C)	None	0	4 μg/g-ash		[56]
	SO_2 added in air	600 mg/Nm^3	5.8 μg/g-ash	increase by 45%	
Lab-scale de novo synthesis experiment (model mixture of Mg–Al–Silicate with carbon passed by air at 300°C)	None	0	33 μg/g-ash		[57]
	SO_2 added in air	600 mg/Nm^3	26 μg/g-ash	decrease by 21%	
Lab-scale de novo synthesis experiment (fly ash passed by air at 350°C)	1% elemental S in fly ash;	n.a.	10.8 μg/g-ash		[58]
	2% elemental S in fly ash	n.a.	19 μg/g-ash	increase by 76%	
Lab-scale 'dioxin formation from precursors' experiment (solid catalyst passed by air with phenol at 300°C)	None	0	0.37 μg/GC-injection		[59]
	SO_2 added in air	1000 ppm	0.32 μg/GC-injection	not significant	
Pilot-scale IFR furnace burning natural gas with MSWI fly ash injection	None	n.a.	2.8 μg/Nm^3		[60]
	SO_2 added in furnace (850°C)	416 ppm	0.4 μg/Nm^3	decrease by 86%	
	SO_2 added in end plate (450°C)	452 ppm	0.8 μg/Nm^3	decrease by 71%	
Pilot-scale fluidized-bed combustor burning mixture of wood and PVC	Gaseous SO_2 310 ppm added	20 ppm	4.5 μg/Nm^3		[61]
	Gaseous SO_2 950 ppm added to fuel	390 ppm	1.8 μg/Nm^3	decrease by 60%	
	Fuel containing 55% coal	250 ppm	0.041 μg/Nm^3	decrease by 99%	
	Fuel containing 56% coal and 0.68% S powder	660 ppm	0.039 μg/Nm^3	decrease by 99%	
Full-scale MSW incinerator testing	SO_2 added to boiler section or sulfur to MSW	200 mg/Nm^3	0.32 μg/Nm^3	decrease by 44%	[1]
		2000 mg/Nm^3	0.18 μg/Nm^3		
Full-scale MSW incinerator testing	None	244 mg/Nm^3	8.3 ng-TE/Nm^3		[62]
	30% lignite in MSW	1581 mg/Nm^3	8.69 ng-TE/Nm^3	not significant	
	60% lignite in MSW	2532	0.91 ng-TE/Nm^3	decrease by 89%	

[a] From Table 7 onward, most of the tables in the paper are for comparison of the effect of a certain operating parameter on PCDD/F levels. The change of the parameter studied is given in the table, all other operating parameters are held constant, and the change in PCDD/F level is always compared with the baseline experiment.

precursors, preventing subsequent chlorination and biaryl synthesis. (4) Lindbauer and co-workers [64,65] proposed that when considering the influence of sulphur compound addition on PCDD/F, the governing parameter is SO_3, not SO_2, and the PCDD/F formation inhibition is by masking of catalytic dust particle surface due to sulphatization with SO_3.

In the opinion of the present authors, the mechanism proposed by Lindbauer et al. is most likely for some reasons, e.g. it is known that sulphur can convert heavy metals into metal sulfides [66] and there are a number of these reactions. More study about the transformation of heavy metals in combustion and the interaction with sulphur and other nonmetallics is needed to fully understand the chemical reactions involved and provide guidance for practical application of the technique.

4.5.2. Alkaline sorbents

Alkaline sorbents are used for control of acidic gas emissions from combustion sources such as coal-burning power stations. Some common sorbents are: CaO, $CaCO_3$, $Ca(OH)_2$, $CaSO_4$, $MgCO_3$, MgO, $Mg(OH)_2$, $MgSO_4$; and less commonly: BaO, $BaCO_3$, $Ba(OH)_2$, $BaSO_4$, $NaOH$, $NaHCO_3$, Na_2CO_3. These sorbents can be added to the combustor or wet/dry scrubber and react with acidic gases to produce solid residues. For example, lime reacts with hydrogen chloride: $Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$, where the products are water and calcium chloride which is a solid and can be captured as bottom ash or fly ash. These sorbents are very effective in removing HCl, HBr, HF, SO_2, etc. If one considers the chlorine levels in flue gases as an important parameter in PCDD/F formation, then the addition of these sorbents should also reduce the PCDD/F levels. So many experimental studies for reducing PCDD/F formation by sorbent injection have been carried out [51,67–73]. The experimental results are, however, controversial. When sorbents were added, the HCl level was always decreased, but the PCDD/F level could be increased, decreased or remain unchanged (Table 8). The reason for this phenomenon is not clear; possibly, the flue gas HCl level is not a controlling factor with respect to PCDD/F formation.

4.5.3. Ammonia

Ammonia injection is often used for the control of NO_x emissions from combustion sources. In selective noncatalytic reduction (SNCR) technology, NH_3 is injected into the high-temperature combustion zone or boiler section; some homogeneous gas-phase reactions (e.g. $6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$) reduce NO into N_2 at reaction temperatures in the range of 850–1100°C. In SCR technology, NH_3 is injected into the low-temperature postcombustion zone, and some heterogeneous catalytic reactions (e.g. $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$) reduce NO into N_2 at reaction temperatures in the range of 320–430°C in the presence of a reduction catalyst. As to the influence of ammonia injection on PCDD/F levels, a number of studies have been reported as listed in Table 9. Significant reduction of PCDD/F formation has been observed in several cases [13,74,75]; insignificant influence has also been reported [1]. It has been postulated that the ammonia may suppress the catalytic activity of fly ash [13,74,75], but the mechanistic details have not been elucidated so far.

Table 8
Effect of sorbent addition on PCDD/F levels

Experiment	Mode and amount of sorbent addition	Flue gas HCl level	PCDD/F level	Change in PCDD/F	Ref.
Full-scale grate-type incinerator	Flue gas cooled in a circulating fluidized-bed of silica sand	n.a.	140 ng/Nm^3		[51]
	Flue gas cooled in a circulating fluidized-bed of limestone	n.a.	27 ng/Nm^3	decrease by 80%	
Full-scale revolving fluidized-bed incinerator	None	380 ppm	9.7 ng/g-boiler ash		[68]
	51 kg-dolomite/t-MSW	170 ppm	9.1 ng/g-boiler ash	not significant;	
	158 kg-dolomite/t-MSW	80 ppm	0.6 ng/g-boiler ash	decrease by 94%	
Full-scale MSW incinerator	None	n.a.	2.84 ng-TE/Nm^3		[69]
	with Mg(OH)$_2$ addition	n.a.	5.53 ng-TE/Nm^3	increase by 95%	
Pilot-scale fluidized-bed combustor	None	520 mg/Nm^3	3.2 μg/Nm^3		[70]
	refuse derived fuel with 15% lime	100 mg/Nm^3	4.25 μg/Nm^3	increase by 33%	

Table 9
Effect of ammonia injection on PCDD/F levels

Experiment	Mode and amount of ammonia addition	PCDD/F level	Change in PCDD/F	Ref.
Lab-scale de novo synthesis experiment (fly ash passed by synthetic gas at 300°C)	None	10.1 μg/g-ash		[74]
	300 mg-NH$_3$/Nm^3 added in the synthetic gas	1.6 μg/g-ash	decrease by 84%	
MSWI flue gas was passed through a 'PCDD/F reactor' kept at 300°C	None			[75]
	NH$_3$ added to the flue gas at NH$_3$/HCl molar ratio 2 or 4		PCDD and PCDF decrease by 94% and 99.9%, respectively	
Full-scale grate-type incinerator	None	6.34 ng-TE/Nm^3 at ESP outlet		[13]
	injecting an aqueous solution of ammonia into the furnace at 900°C	0.91 ng-TE/Nm^3 at ESP outlet	decrease by 86%	
Full-scale incinerator	None	320 ng/Nm^3	not significant	[1]
	injection of NH$_3$ (3000 mg/Nm^3) into boiler section	400 ng/Nm^3		

Table 10
Inhibition of 'precursor formation' of PCDDs (in all experiments fly ashes deposited with pentachlorophenol were passed by air at 300°C for 1 h)

Nature, amount (wt.% of fly ash) and mode of inhibitors added	PCDD formed (ng/100 μg of precursor)	PCDD reduction (%)	Ref.
None	5472		[84]
Inhibitor (1.6%) added by solution impregnation to fly ash:			
2-aminoethanol	16	99.7	
triethanolamine	24	99.6	
urea	451	91.8	
pyridine fraction	731	86	
ethan-1,2-diol	808	85	
3-aminopropanol	873	84	
quinoline fraction	930	83	
ammonia sulfide	1511	72	
hexamethyldisilazane	3795	30	
triethylamine	3981	27	
cyanamid	5165	5	
None	2693		[84]
Ethylene glycol (1%) added by solution impregnation to fly ash	996	63	
None	2194		[84,80]
Calcium oxide (2%) mixed manually with fly ash	322	85	

None	2000		[82]
Inhibitor added by solution impregnation to fly ash:			
triethanolamine (2%)	40	98	
monoethanolamine (2%)	50	97	
monoisopropanolamine (2%)	40	98	
triethanolamine + KOH (2:8) (4%)	50	97	
triethanolamine + NaOH (2:8) (4%)	20	99	
Fly ash without inhibitor	10		[83]
Fly ash with HNO_3 injected to the gaseous reactant stream (25 wt.% of the gas)	0.4	96	
Exhausted fly ash without inhibitor	12		
Exhausted fly ash with H_2SO_4 injected to the gaseous reactant stream (25 wt.% of the gas)	120	increase	
Fly ash without inhibitor	220		
Fly ash with NH_4OH injected to the gaseous reactant stream (20 wt.% of the gas)	48	78	
100 μl of thiophene added to fly ash	n.a.	significant reduction for lower chlorinated PCDDs	[85]
7 ml of carbon disulphide added to fly ash	n.a.	significant reduction	

Table 11
Inhibition of 'de novo synthesis' of PCDD/Fs

Experiment	Nature, amount and mode of inhibitors added	PCDD/F formation (ng/g-ash)	PCDD/F reduction (%)	Ref.
Fly ash was passed by air at 300°C for 2 h	No inhibitor	8483		[28]
	Fly ash pretreated with hydrogen sulfide in water	547	93	
Fly ash with activated carbon was passed by air at 348°C for 1 h	None	5.57[a]		[86]
	Inhibitor (2%) mixed in fly ash:			
	ethylenediaminetetraacetic acid	1.36[a]	75	
	nitrilotriacetic acid	1.12[a]	80	
	Na_2S	1.1[a]	80	
	$Na_2S_2O_3$	3.87[a]	30	
Heat treatment of fly ash at 350°C	None	2099		[79]
	with PSEGC[b]	248	88	
	with SMEGC[b]	422	80	

[a] In nmol/g of fly ash.
[b] The composition of the inhibitors was not disclosed.

4.5.4. Hydrogen peroxide and ozone

Hydrogen peroxide and ozone are strong oxidants and are expected to oxidize organic compounds (including PCDD/F) in flue gases when added to the postfurnace zone of incinerators. Some studies about this technique have been reported [76,77]. Vogg et al. [76] added 80 mg-H_2O_2/Nm^3 to the flue gas before a multiple cyclone at a point where the temperature is 200 to 250°C, and found that the PCDD/F level decreased from 440 ng/Nm^3 at the cyclone inlet to 1.5 ng/Nm^3 at the cyclone outlet in one experiment, and from 98 ng/Nm^3 at the cyclone inlet to 46 ng/Nm^3 at the cyclone outlet in another experiment when the solid phase PCDD/F were also included.

4.6. PCDD / F formation inhibitors

Techniques for inhibition of fly ash catalytic activity in PCDD/F formation through the addition of organic chemicals have been studied actively by Karasek and Naikwadi [78], Naikwadi and Karasek [79,80], Beard et al. [81], Naikwadi et al. [82], Ross et al. [83], Dickson et al. [84], Karasek et al. [85] and others [28,86,87]. When comparing the experimental data, a distinction among 'de novo synthesis' experiment, 'precursor formation' experiment and real incinerator testing should be useful as 'de novo synthesis' and 'precursor formation' have different reaction pathways, so that the same chemical reagent tested may exhibit different inhibitory effects or act on different mechanisms in different experimental conditions. Thus in Tables 10–12, the experimental data are compiled according to 'de novo synthesis' experiment, 'precursor formation' experiment and full-scale incinerator testing, respectively.

A variety of chemicals have been shown to possess some kind of inhibiting effect on PCDD/F formation. The most effective inhibitors for PCDD formation from aromatic precursors are triethanolamine and 2-aminoethanol shown in Table 10. The mechanisms of the inhibitory action of these chemicals have not been elucidated to a significant extent. Presumably, the hydroxy-functional group present in the inhibitors renders an easier adsorption of these chemicals on the fly ash surfaces, and the amino-functional group may form some surface complexes with the metal species in the fly ash (e.g. surface imine, aldehyde, cyanide and/or axide groups [87]), whereas the sulphur in CS_2

Table 12
Inhibition of PCDD/F formation in full-scale incinerator[a] [78]

Inhibitors added	PCDD/F level			PCDD/F reduction (%)		
	Fly ash (ng/g)	Raw gas (ng/Nm^3)	Clean gas (ng/Nm^3)	Fly ash	Raw gas	Clean gas
None	230	49.7	53.9			
with PSEGC	44	80.2	39.3	81	increase	27
None	230	100.8	82.9			
with SMEGC	42	247.8	32.9	82	increase	60

[a]A mixture of inhibitor/destroyer and water was used; the destroyer was injected in the temperature window of 590 + 50°C, the inhibitor injected in the temperature window of 375 + 50°C. The amount of each of inhibitor and destroyer was 7–10% of the fly ash, and the amount of water was 13 times that of inhibitor or destroyer.

[85], H_2S [28] and Na_2S [86] may form sulphates with the metal species in the fly ash. All these actions may reduce the available catalytic metallic sites on fly ash and hence the PCDD/F formation. The amount of inhibitors added to fly ash appears to be high in these experiments and the addition method is often by solution impregnation to fly ash prior to the experiment. In some cases the inhibitors might have simply been coated on the fly ash surfaces and prevent chemical reactions to occur by this physical deposition rather than by poisoning of catalytic sites. The full-scale incinerator experiment by Karasek et al. seems to be a partly success (Table 12). The PCDD/F levels in fly ashes were decreased by 80%, but the PCDD/Fs in raw gases were increased by a factor of 2, and the PCDD/Fs in clean gases were decreased by 30–60%.

Even though some chemical reagents can be found to be effective in inhibiting PCDD/F formation in laboratory experiments, for a real incinerator it is very difficult to deliver the chemical reagents to the fly ash surfaces as the fly ashes are generated freshly and continuously from the combustor; a large amount of inhibitor solution may be required due to mixing the mass transport limitations. The unadsorbed/unreacted inhibitors present in flue gas could also cause problems as some inhibitors are toxic themselves or can be transformed into other organic/inorganic chemicals which are toxic/corrosive.

4.7. Discussion

The control of PCDD/F formation in the postcombustion region of incinerators is a very difficult technical field. The success of the development of control techniques depends fundamentally on our understanding of the physical and chemical processes involved in PCDD/F formation in a real incinerator. The present theory of PCDD/F formation tells us that PCDD/F are formed through certain heterogeneous catalytic reactions between flue gas and fly ash (or certain metallic components in the fly ash) in the temperature range 200–500°C. Therefore, the techniques in Section 4.2 'Control of the temperature-time profile of flue gases' attempt to lower the temperature of the flue gas rapidly to below 200°C and hence decrease the PCDD/F formation. The techniques in Section 4.3 'High-temperature separation of fly ashes' attempt to reduce the amount of fly ashes in the critical temperature range and thus decrease the PCDD/F formation. The techniques in Section 4.4 'Boiler design and soot blowing' attempt to reduce the residence time of fly ashes in the temperature range concerned and hence the PCDD/F generation. The techniques in Section 4.5 'Injection of inorganic additives' include application of sulphur compounds which is meant to reduce the chlorination agents Cl_2, alkaline sorbents which is to reduce the HCl level, ammonia which is said to inhibit the catalytic activity of fly ash, and hydrogen peroxide and ozone which are strong oxidants and in general reduce the organic compound emissions. Finally, the techniques in Section 4.6 'PCDD/F formation inhibitors' attempt to introduce some chemical reagents into the flue gas stream to poison the catalytic sites on fly ashes. In spite of these great research efforts, there is still no reliable method that can control the formation of PCDD/Fs in the postcombustion region of incinerators due to incomplete understanding of the mechanisms of PCDD/F formation in incinerator conditions as well as a number of technical difficulties.

5. Combustion measures to reduce PCDD/F formation

5.1. Background

Although PCDD/F are known to be formed in the postcombustion zone of incinerators, the reactants or precursors for PCDD/F formation are generated in the combustor itself. The temperature profile and flue gas residence time in the postcombustion zone are also influenced by the combustion. Thus it is expected that combustion conditions have major influences on PCDD/F formation levels in incinerators, and combustion measures such as optimization of combustion parameters and improved design of furnace structures could be useful in reducing PCDD/F formation.

5.2. Optimization of combustion parameters

When some PCDD/F measurement data are obtained in different incinerator studies, it is possible to compare these data and select a type of incinerator or a set of design parameters that has the minimum PCDD/F formation. For a specific incinerator, it is also possible to compare the PCDD/F measurement data under different operating conditions and select a set of operating parameters that has the minimum PCDD/F formation. This is concerned with the optimization of combustion parameters for the minimization of PCDD/F formation and has been one of the research objectives of many incinerator testing programmes. A large number of publications concerning the relationship between combustion conditions and PCDD/F emissions can be found in the literature. Before discussing these findings the following points are worthy of noting.

(1) Experimental error: The analytical uncertainty for PCDD/F was $\pm 100\%$ before 1990, and $\pm 30\%$ after 1990 in a major research laboratory. Considering also the uncertainty in the measurement of other combustion parameters, the experimental error in incinerator studies is large. Sometimes a difference of PCDD/F data by a factor of 2 could be considered to be within the experimental error if the experimental error has not been estimated and reported by the investigator.

(2) Data analysis method: PCDD/F formation in combustion processes is influenced by a variety of combustion parameters simultaneously and is regarded as a multivariate process. Some data analysis methods such as Pearson coefficients, simple regression and scatter plot are useful only for initial data exploration. Multivariate data analysis methods such as principal component analysis and multiple regression analysis are needed in order to find the optimum operating condition with minimum PCDD/F formation.

(3) Averaging parameters: PCDD/F sampling is usually done continuously for a period of 4 h. During this period, combustion parameters may not be held constant, and the influence of transition, unsteady state of combustion is difficult to control and estimate.

(4) 'Memory effect': This means a carryover of the effect of certain operating parameters on PCDD/F during different experimental runs. The 'memory effect' is significant in real incinerator testing; in some study no correlation is found between a certain combustion parameter and PCDD/F, this is sometimes due to the 'memory effect'. The reason for the 'memory effect' is not known for certain; it may originate

Table 13
Correlation between combustion parameters and PCDD/F emissions

Experiment/author	O_2	CO	HCl	SO_2	Furnace temperature	Fly ash loading	Cu	Ref.
Environment Canada (Quebec City)	n.a.	+	0	+	0	+ +	+ +	[88]
Hasselriis	Min PCDD/F at 7% O_2	Min PCDD/F at 10 ppm	n.a.	n.a.	Min PCDD/F at 900℃	n.a.	n.a.	[89]
German test programme	+	+	0	−	−	+	n.a.	[1]
UK test programme	n.a.	0	0	+	−	0	+ +	[90]
Dutch test programme	+	0	+ +	0	n.a.	+ +	n.a.	[91,92]
Pilot fluidized-bed combustor	+ +	0	0	n.a.	+ +	n.a.	n.a.	[70]
Innovative furnace reactor	Max PCDD/F at 5% O_2	n.a.	+	n.a.	n.a.	n.a.	n.a.	[67]

+ +: Significant positive correlation.
+: Positive correlation.
0: No correlation.
−: Negative correlation.
− −: Significant negative correlation.

from the adsorption–desorption of PCDD/Fs or the deposition of particulate matter on the wall of the boiler and APCDs.

For the above difficulties an incinerator testing programme studying the relationship between combustion parameters and PCDD/F formation must be carefully planned using experimental design and conducted with measures to prevent 'memory effects' and maintain steady-state operation, and the resulting data should be analyzed using multivariate statistical methods. However, due to the high cost of incinerator testing and PCDD/F analysis, these were not always possible.

In Table 13, some results of the correlation studies in major incinerator testing programmes are compiled. It seems that the results from different testing programmes are contradictory. For example, about the influence of flue gas O_2 level on PCDD/Fs, Lenoir et al. [70] found that high O_2 values increased the dioxin levels, but Vogg et al. [76] reported that increasing specific air consumptions were correlated with decreasing dioxin levels. Hasselriis [89] found that there exists an optimum O_2 level between 6% to 9% with minimum PCDD/F formation, but Gullett et al. [67] suggested that intermediate levels of O_2 (4% to 7%) tend to produce larger PCDD/F yields than the extremes. For HCl, some researchers found a correlation with PCDD/F, but others did not. For SO_2, positive, negative and no correlation have all been reported.

In view of the complexity of the PCDD/F formation process, particularly the multi-stage nature of the process (i.e. the precursors are generated in the combustion zone, then PCDD/F are formed in the postcombustion zone) and that many kinds of reactants and catalysts are involved in the reactions, it may not be a surprise that the relationship between combustion conditions and PCDD/F levels are so complex and controversial. It is possible that different types of incinerators have quite different behaviour, and no general, universally applicable correlationship can be found. Mechanistic explanation for these correlation studies are very difficult to give because the knowledge about the PCDD/F formation processes in an actual incinerator is not complete at present.

5.3. Advanced combustor design

There are a number of different combustor designs and structures ranging from grate-type to fluidized-bed, from two-stage combustion to vortex flow or swirl combustor. In general, the furnace structures having a higher degree of turbulence and mixing should lead to better combustion and lower emission levels of products of incomplete combustion. Hiraoka and Okajima [4] gave an example about how the furnace structure affects PCDD/F formation. In an old plant, the PCDD/F measurements were 40, 32, 43 ng-TE/Nm^3 at furnace outlet, ESP inlet and outlet, respectively. After installing nose sections and secondary air nozzles in the furnace, the PCDD/F measurements were decreased to 4, 15, 26 ng-TE/Nm^3 at furnace outlet, ESP inlet and outlet, respectively. The PCDD/F emission reduction by improvement of furnace structure was very remarkable in this case.

Under ideal conditions if the combustion in the furnace is so complete that only water and carbon dioxide are combustion products, then there should be very little PCDD/F formation in the postfurnace region. Three examples attempting to utilize this concept of

advanced combustor design to control PCDD/F formation have been given in the DIOXIN'94 Symposium. Fleck [93] reported the development of a Vortex-secondary combustion chamber with staged and tangential secondary air injection; the PCDD/F stack measurements in this facility were extremely low. Kato et al. [94] reported experiments conducted in incinerator models with different flow patterns. The model with eccentric inlet and axial-flow outlet was found to have the lowest CO (< 2 ppm) and PCDD/F levels (0.05 ng-TE/Nm^3) in the furnace outlet. However, the PCDD/F levels were found to increase again in the postfurnace zone and reached 2.52 ng-TE/Nm^3 at gas cooler outlet where the temperature was 210°C. This represented the reformation of PCDD/F by a factor of 50 in the postcombustion zone for this incinerator model with only 2 ppm CO emission. Asai et al. [95] and Watanabe et al. [96] reported experiments in an advanced fluidized-bed swirl incinerator for complete combustion. The CO levels were < 1 ppm in many experimental runs, the PCDD/F levels were 0.18 ng-TE/Nm^3 at furnace outlet. However, the reformation of PCDD/F still occurred in the low-temperature postcombustion zone of this incinerator; in one case the PCDD/F level reached 0.8 ng-TE/Nm^3 at gas cooler exit, and 2.1 ng-TE/Nm^3 at induced draft fan exit. This represented the reformation of PCDD/F by a factor of 10 in the postcombustion zone for this advanced swirl fluidized-bed incinerator with 0–1 ppm CO emissions.

The above data illustrated that the de novo synthesis of PCDD/F is a very peculiar, persistent phenomenon. Even for these advanced combustors with CO levels as low as nearly zero (the CO levels can usually be regarded as a good indicator for the completeness of combustion), the de novo synthesis has not be decreased by a significant extent. The present theory of PCDD/F formation does not seem to be sufficient to explain this.

5.4. Automatic combustion control systems

Combustion stability has a great influence on PCDD/Fs; 'bad combustion' as indicated by the appearance of CO peaks were observed to cause about 10 times higher PCDD/F emissions than normal combustion [54,97]. The installation of automatic combustion control systems is useful to maintain stable combustion and to reduce PCDD/F formation [4,98,99]. At present on-line analysis and monitoring of PCDD/F are still not possible, so no combustion control system dedicated to PCDD/F reduction is available. In this respect some PCDD/F prediction and control models of an empirical nature developed for a specific type of incinerator could be of value [100].

5.5. Additive injection

Many additives discussed in Sections 4.5 and 4.6 can also be used in the combustion chamber.

5.6. Discussion

Combustion measures are regarded as the primary measures to control PCDD/F formation. In the past the 3 T's principle (temperature, time and turbulence) has been

widely discussed and it has been suggested that a long flue gas residence time at high combustion temperature with intensive turbulence mixing is sufficient to destroy the organic pollutants. However, with respect to PCDD/Fs the 3 T's principle does not seem to be able to ensure that PCDD/Fs are not formed. How to reduce PCDD/F formation through combustion measures such as optimization of combustion parameters is not entirely clear at present. More experimental and theoretical study about the mechanisms, kinetics and mathematical models of dioxin formation in combustion processes is needed to provide guidance for practical work.

6. Control of waste composition and properties

6.1. Background

The control of waste composition and properties may provide a means to control dioxin pollution from waste incinerators, because if the precursor compounds for PCDD/F formation are identified and separated from the waste stream, then PCDD/F emissions may be eliminated to a large extent. This section discusses this option briefly.

6.2. PVC and PCDD/F

The relationship between PVC and PCDD/F has been a controversial issue for a long time. The presence of PVC in municipal wastes has increased the chlorine content of the wastes considerably and has been suspected to be one of the causes for the high PCDD/F emissions from municipal waste incinerators. Past studies on this issue were done by: (a) in a laboratory-scale or a real incinerator, artificially adjust the PVC content of the fuel and observe the change of the PCDD/F emission levels; and (b) study the correlationship between flue gas HCl concentration and PCDD/F emission levels. About half of the past studies found a positive correlationship between PVC and PCDD/F, another half found no correlationship, reviewed in Ref. [101]. The recent opinion on this issue tends to be that PVC present in municipal wastes in the normal amount of about 1 wt.% has no significant influence on PCDD/F emissions, and separation of PVC from municipal waste stream is not likely to reduce PCDD/F emissions from incinerators because of the presence of inorganic chlorine sources in the wastes.

6.3. Refuse derived fuels

Municipal solid wastes may be mass-burned or processed into refuse derived fuels (RDF) in a waste treatment plant. A typical RDF plant separates and recovers a large portion of the plastics, ferrous and aluminium metals, cardboard, paper, glass, etc. using separation equipments such as shredders, air classifiers, magnetic separators and also manual sorting. After the recovery of these useful materials the rest of the municipal wastes may be converted into RDFs. Compared with municipal wastes, RDFs are relatively homogeneous fuels in terms of size, composition and energy content and have

a somewhat lower metal content. It is possible that RDF combustion generates less dioxins than mass burn of MSW because of the more favourable combustion condition and lower metal content in RDF (metals such as Cu and Fe are known to catalyze PCDD/F formation). However, no comparative data are available to verify this.

6.4. Additives

Many additives discussed in Sections 4.5 and 4.6 can also be mixed with municipal wastes and fed into the combustion chamber.

6.5. Discussion

What are the precursor compounds in municipal wastes for PCDD/F formation is still not known for certain. The PVC content of municipal wastes may not be a significant factor. Perhaps the reason for the high PCDD/F formation in MSWI is that municipal wastes contain a lot of man-made materials which are usually high in aromatic composition and lead to higher levels of aromatic compounds emissions when burnt. The extremely variable properties and high metal content of municipal wastes are probably other factors. Measures that make the fuel properties more uniform such as multi-stage shredding and mixing and separate out the metals from the fuels could be helpful in controlling PCDD/F formation.

7. Conclusions

The state of the art for PCDD/F formation and emission control in municipal solid waste incineration has been reviewed in this article. The emission standard of 0.1 ng-TE/Nm^3 can be met in a modern incineration plant through emission control measures, e.g. activated carbon injection and fabric filtration as currently practiced in many installations. These PCDD/F emission control measures, however, have increased the cost of municipal waste incineration and also led to the discharge of a larger amount of solid residues from incineration plants. A more fundamental approach is to control the formation of PCDD/Fs in incineration processes. In this approach measures may be taken in the postcombustion zone, the combustion chamber and the waste feeding. A variety of techniques have been attempted in the past as discussed in the major sections of this article. However, no proven technique is available at present to prevent the formation of PCDD/Fs in the low-temperature postcombustion region of incinerators (currently in a typical waste heat boiler the PCDD/F concentration at boiler inlet is 1 ng-TE/Nm^3 and at boiler outlet is 5 ng-TE/Nm^3 due to the de novo synthesis of PCDD/Fs in the boiler section). In future technological development the primary objective should be to suppress the de novo synthesis of PCDD/Fs in the boiler section. In this aspect the most promising directions appear to be: injection of inorganic additives into the combustor and boiler section, prevention of soot deposition in the heat surfaces, high-temperature filtration of fly ashes using cyclone and ceramic filtration, advanced combustor design and structure optimization, installation of automatic combustion

control systems, and maintaining uniform waste composition and feeding. A critical problem in future development is that the present theory of PCDD/F formation in combustion processes is incomplete or inaccurate in part. The theory does not provide an unambiguous, comprehensive picture of the PCDD/F formation processes in actual incineration plants, and cannot explain the observed complex relationship between combustion conditions and PCDD/F formation. As the basic theory of PCDD/F formation is advanced, a better guidance to incinerator designers and operators about how to control PCDD/F formation may be expected in the future.

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