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Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: review

Gordon McKay

Department of Chemical Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

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Abstract

The present review discusses the current views on methods to minimise dioxins, namely polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs), formation in MSW incineration systems. The structure of this group of compounds is discussed initially and then the toxic equivalence scale is presented for the most common isomers and congeners in the dioxin family. The current status on dioxin limits imposed in various countries and by various organisations is presented. A detailed analysis of the theories leading to dioxin formation in MSW incineration is given, since, this has been one of the most controversial areas of dioxin chemistry for the past 20 years.

Three dioxin formation theories were considered possible for a long time; (i) from PCDD/PCDFs originally present in the furnace feedstock; (ii) from precursor compounds (foundation formatting molecules which could react rapidly with other groups in the system to form dioxins) in the MSW feed; (iii) from de novo synthesis of smaller, relatively innocuous chemical molecules combining together to form the dioxins. Methods (ii) and (iii) are based on heterogeneously catalysed reactions. Some researchers are considering possible homogeneous thermal reaction formation of dioxin.

This review demonstrates that with the advanced modern MSW combustion systems, option (i) is a most unlikely route and also methods (ii) and (iii) are quite feasible. Based on thermodynamic and kinetic data in the literature, the rate and extent of the formation of dioxins and their precursors by certain mechanisms can definitely be contributing to routes (ii) and (iii). Since even the most advanced MSW combustion systems do not produce complete combustion, predominantly because of inadequate feed preparation and turbulence, some de novo synthesis of precursors can also take place.

These ‘de novo precursors’ could be carried through the combustion unit adsorbed or absorbed on particulate material such as soot and dust, but also these precursors could be formed during the cooling process by heterogeneous catalytic reactions and go on to form dioxins. The maximum rate of formation of PCDD/PCDFs from both sources lies in the temperature range 300–400 °C. This knowledge of formation rates and mechanisms provides the basis of designing combustion systems. A two stage approach is adopted; firstly, system design to achieve complete combustion and minimise formation; secondly, end-of-pipe treatment systems to remove dioxins.

In the first case, combustion temperature should be above 1000 °C, combustion residence time should be greater than 1 s, combustion chamber turbulence should be represented by a Reynolds number greater than 50,000, good MSW feed preparation and controlled feed rate are also critical. In the second category, very rapid gas cooling from 400 to 250 °C should be achieved, semi-dry lime scrubbing and

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Abbreviations: AC, activated carbon; ACSS, activated carbon scrubbing solution; APCD, air pollution control device; APME, Association of Plastics Manufacturers in Europe; ASME, American Society of Mechanical Engineers; BF, bag filter; BPM, best practical means; COT, UK Committee on Toxicology of Chemicals in Food, Consumer Products and Environment; CTZ, critical temperature zone; DOE, Department of the Environment, UK; DIAC, direct injection of activated carbon; DS, dry scrubber; DSI, dry sorbent injection; EADON, toxic equivalence factors proposed by Eadon method; EEC, European Economic Community; EGB, electro granular bed; ESP, electrostatic precipitator; FF, fabric filter; FRG, Federal Republic of Germany; GCP, good combustion practice; HMIP, Her Majesty’s Inspectorate on Pollution, UK; HOC, hearth-oven coke; HRGC, high resolution gas chromatography; HRMS, high resolution mass spectrometry; IARC, International Agency for Research on Cancer; K_{ow}, octanol-water partition coefficient; MSW, municipal solid waste; MSWI, municipal solid waste incinerator; NATO, Northern Atlantic Treaty Organisation; NOAEL, no observed adverse effect level; OCDD, octachlorinated dibenzodioxin; OCDF, octachlorinated dibenzofuran; PCB, polychlorinated biphenyls; PCCS, programmable computer control system; PCDD, polychlorinated dibenzodioxin; PCDF, polychlorinated dibenzofuran; PCP, pentachlorophenol; RDF, refuse derived fuel; SCR, selective catalytic reduction/reactor; SDA, spray dry absorber; TALuft, Technische Airbildung Luft; TCDD, tetrachlorinated dibenzodioxin; TCDF, tetrachlorinated dibenzofuran; TDI, tolerable daily intake; TEF, toxic equivalence factor; TEQ, toxic equivalence; USEPA, United States Environmental Protection Agency; WHO, World Health Organisation; WQ, water quench; WS, wet scrubber

E-mail address: kemckayg@ust.hk (G. McKay).

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bag filtration coupled with activated carbon injection adsorption as end-of-pipe treatments can all play a role in prevention or minimisation of dioxins in the final flue gas emission to the atmosphere.

Keywords: Municipal solid waste incineration; Polychlorinated dibenzodioxins; Polychlorinated dibenzofurans

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1. Introduction

The demands of our society generate wastes that tend to increase in quantity as the standard of living increases. The most effective means of dealing with the problem is to reduce the amount of wastes generated. The trend with continually improving living standards has been contrary to this. The opportunities for landfilling as a disposal method for municipal solid waste (MSW) are rapidly declining with depleting available cheap land resources and the wasteful nature of disposing useful resources in the landfill operation. The options for public sector waste reduction translate into separation, recycling and resource recovery. Due to the limited economic benefits of separation and recycling, resource recovery in the form of heat and power production has gained favour in the past 20 years [1]. During this period incineration of MSW has seen turbulent times in terms of popularity, but it is an attractive alternative for disposal and has significant benefits [2].

- The volume and mass of MSW is reduced to a fraction of its original size (by 85–90% by volume).
- The waste reduction is immediate and not dependent on long biological break-down reaction times.
- Incineration facilities can be constructed closer to the MSW sources or collection points, reducing transportation costs.
- Using heat recovery technology, the cost of the operation can be offset by energy sales.
- Air discharges can be controlled to meet environmental legislative limit values.

However, incineration does have its problems and consequently its critics due to the following reasons.

- Some materials should not be incinerated because they are more valuable for recycling, they are non-combustible or their by-products may give rise to harmful emissions.
- Poor operating practices and the presence of chlorine in the MSW may lead to emissions containing highly toxic dioxins and furans.
- The control of metal emissions may be difficult for inorganic wastes containing heavy metals, such as arsenic, cadmium, chromium, copper, lead, mercury, nickel, etc.
- Incinerators require a high capital costs and trained operators leading to moderately high operating costs.
- Supplementary fuels are required to achieve the necessary high combustion temperatures.

The review focuses on the topic of dioxins and furans, due to their high degree of toxicity and the public indignation and outcry they generate. “Dioxin” is the second most immotively used pollutant terminology expression after “nuclear accident”. This review presents a general review of information concerning dioxin formation and minimisation issues from MSW incinerators. The structures and properties of the dioxins (polychlorinated dibenzo-*para*-dioxins or PCDDs) and furans (polychlorinated dibenzo-*para*-furans or PCDFs) are presented. A review of the sources and origins of PCDDs/PCDFs is given followed by sections on toxicity and health issues, highlighting the justification for concern regarding the production and emission of these compounds. The current status on dioxins emission limits is presented followed by a detailed discussion on the emissions of dioxins from incinerators and in particular, their formation in MSW incinerators. The final section of the review concentrates on the various methods and approaches to dioxin minimisation during incineration and end-of-pipe treatment methods.

2. Dioxins and benzofurans

2.1. *Chemical structures and properties*

Dioxin is one of the most toxic chemicals known. A report released for public comment in September 1994 by the US Environmental Protection Agency [3,4] clearly describes dioxin as a serious public health threat in the 1960s. According to the EPA report, not only does there appear to be no “safe” level of exposure to dioxin, but levels of dioxin and dioxin-like chemicals have been found in the general US population that are “at or near levels associated with adverse health effects”. The EPA report confirmed that dioxin is a cancer hazard to people, that exposure to dioxin can also cause severe reproductive and developmental problems (at levels 100 times lower than those associated with its cancer causing effects); and that dioxin can cause immune system damage and interfere with regulatory hormones.

Dioxins, as they are commonly called, are PCDDs and PCDFs are compounds with similar chemical properties. Each compound comprises two benzene rings interconnected by oxygen atoms. In the case of PCDDs, the benzene rings are joined by two oxygen bridges, and in the case of the PCDFs, the benzene rings are connected by a carbon bond and an oxygen bridge. Fig. 1a and b show the generic structures of PCDDs and PCDFs, respectively. Much of the environmental behaviour of polychlorinated biphenyls (PCBs) can be related to their physical characteristics. The non-polar nature of PCBs means that they are strongly hydrophobic and thus strongly lipophilic. They exhibit a high predilection for smooth surfaces, and combined with their lipophilic and hydrophobic properties, this explains their

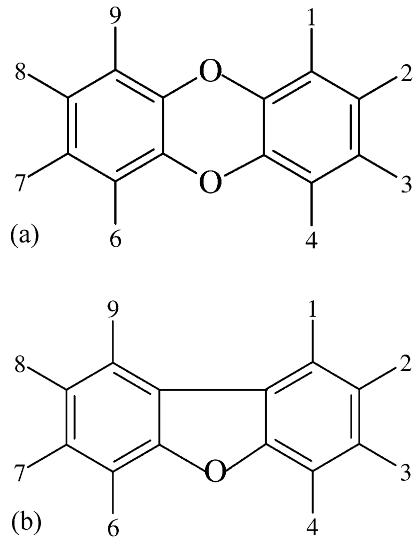

Fig. 1. (a) Dibenzo-*para*-dioxin; (b) dibenzofuran.

presence absorbed on to soil and sediment particles. The high surface concentration of lipids and organic compounds tend to concentrate and stabilise PCBs on the surface of water bodies. All PCDDs and PCDFs are organic solids with high melting points and low vapour pressures. They are characterised by extremely low water solubilities, and have a tendency for being strongly adsorbed on surfaces of particulate matter. The water solubility of dioxin and furans decreases and the solubility in organic solvents and fats increases with increasing chlorine content.

Some of the key properties of the dioxins are presented in Table 1 and full physico-chemical properties have been reviewed [3,5]. There are 75 PCDDs and 135 PCDFs, each differing in the number and position of the chlorine atoms. Each individual PCDD or PCDF is termed a congener (giving 210 in total), while groups of congeners with the same number of chlorine atoms are called homologues. The number of congeners in each homologue group is shown in Table 2. The homologue groups are often abbreviated for convenience; for example, tetrachloro CDDs and CDFs (PCDD/Fs with four substituted chlorine atoms) are abbreviated to TCDDs and TCDFs, respectively, while the fully chlorinated octachloro congeners (eight substituted chlorine atoms) are abbreviated to OCDD and OCDF, respectively.

Table 2
Homologues and congeners of PCDDs, PCDFs and PCBs

Homologue (abbreviation)	Number of congeners		
	PCBs	PCDDs	PCDFs
Monochloro (M)	3	2	4
Dichloro (D)	12	10	16
Trichloro (Tr)	24	14	28
Tetrachloro (T)	42	22	38
Pentachloro (Pe)	46	14	28
Hexachloro (Hx)	42	10	16
Heptachloro (Hp)	24	2	4
Octachloro (O)	12	1	1
Nonachloro	3		
Decachloro	1		
Total	209	75	135

2.2. Dioxin emission sources

The recent concern regarding dioxins developed from their identification in incineration products about 25 years ago. The PCDD and PCDF compounds were reported as being detected in Dutch [6] and in Swiss [7] incinerator fly ash samples. In recent years particularly with advances in analytical chemistry techniques, the measurement of dioxin concentrations has become easier and more reliable, particularly using high resolution mass spectrometry–high resolution gas chromatography (HRMS–HRGC). Analytical and sampling protocols are described in detail in method 23 in [8].

In 1980, following the identification of PCDDs and PCDFs in a wide range of environmental samples in both remote and industrially developed locations in the United States, the Dow Chemical Corporation [9] proposed the trace chemistries of fire hypothesis for their formation and occurrence. This hypothesis stated that in any situation where chlorine, carbon, hydrogen and oxygen came into contact with heat, PCDD/Fs could be formed as trace by-products.

Table 1
Typical physico-chemical properties of PCDD/Fs

Homologue group	Vapour pressure (mmHg at 25 °C)	$\log K_{ow}$	Solubility ($mg\,l^{-1}$ at 25 °C)	Henry's constant
TCDD	8.1×10^{-7}	6.4	3.5×10^{-4}	1.35×10^{-3}
PeCDD	7.3×10^{-10}	6.6	1.2×10^{-4}	1.07×10^{-4}
HxCDD	5.9×10^{-11}	7.3	4.4×10^{-6}	1.83×10^{-3}
HpCDD	3.2×10^{-11}	8.0	2.4×10^{-6}	5.14×10^{-4}
OCDD	8.3×10^{-13}	8.2	7.4×10^{-8}	2.76×10^{-4}
TCDF	2.5×10^{-8}	6.2	4.2×10^{-4}	6.06×10^{-4}
PeCDF	2.7×10^{-9}	6.4	2.4×10^{-4}	2.04×10^{-4}
HxCDF	2.8×10^{-10}	7.0	1.3×10^{-5}	5.87×10^{-4}
HpCDF	9.9×10^{-11}	7.9	1.4×10^{-6}	5.76×10^{-4}
OCDF	3.8×10^{-12}	8.8	1.4×10^{-6}	4.04×10^{-5}

Many natural sources can release dioxins. For instance, before the large-scale manufacturing and use of chlorinated chemicals, the presence of these compounds was confirmed [10–12] in historical times. Biological formation of PCDDS and PCDFs in sediments and soils, especially forest soils and sediments [13,14] has been confirmed. Examination of PCDD/F congener profiles in uncontaminated forest soils and sediments and comparison with those of known sources has suggested that the presence of PCDD/Fs in these samples cannot be readily explained by inputs from man-made sources [15]. Oberg and co-workers [16–18], and Schramm et al. [19] have also noted the potential for the natural formation of PCDD/Fs in sewage sludge and compost under normal environmental conditions; these are synthesised by peroxidates from chlorinated organic precursors such as chlorophenols. An extensive series of papers by Gribble [20–23] describes the formation of organohalogens, particularly chlorophenols and dioxins, by synthesis from natural sources.

Since the 1930s, there has been a steady increase in environmental levels of dioxins coinciding with the large-scale production and use of chlorinated chemicals [11,24]. Man-made sources of PCDD/Fs can be divided into a number of main categories [25] and countries are now beginning to compile data and establish dioxin inventories. The USEPA [4,26] have derived these emission estimates and identified the following major sources of dioxin releases in the USA.

2.2.1. *Combustion sources*

PCDD/PCDFs are formed in most combustion systems. These can include waste incineration (such as MSW, sewage sludge, medical waste, and hazardous wastes), burning of various fuels, such as coal, wood, and petroleum products [27–29] other high temperature sources such as cement kilns, and poorly controlled combustion sources such as building fires, burning any chlorine compounds [29–31].

2.2.2. *Metal smelting and refining sources and processing sources*

PCDD/PCDFs can be formed during various types of primary and secondary metals operations including iron ore sintering, steel production, and scrap metal recovery [32].

2.2.3. *Chemical manufacturing*

PCDD/PCDFs can be formed as by-products from the manufacture of chlorine bleached wood pulp [33] and chlorinated phenols, e.g. pentachlorophenol (PCP) [16,17,34,35], PCBs, phenoxy herbicides (e.g. 2,4,5-trichloro-phenoxy-acetic acid), and chlorinated aliphatic compounds (e.g. ethylene dichloride).

2.2.4. *Biological and photochemical processes*

Recent studies have suggested that PCDD/PCDFs can be formed under certain environmental conditions, e.g. composting [36] from the action of microorganisms on chlorinated phenolic compounds. Similarly, PCDD/PCDFs have been reported to be formed during photolysis of highly chlorinated phenol [37].

2.2.5. *Reservoir sources*

Reservoirs are material or pieces which contain previously formed PCDD/PCDFs or dioxin-like PCBs and have been the potential for redistribution and circulation of these compounds into the environment. Potential reservoirs include soils, sediments, vegetation, and PCP-treated wood [38,39]. Recently, PCDD/PCDFs have been discovered in ball clay deposits. Although the origin of the PCDD/PCDFs in these clays has not been confirmed, natural occurrence is a possibility.

The procedures and results of the US inventory are consistent with the published national inventories for several European countries. Air emission estimates reported for West Germany [28]; Austria [40]; The Netherlands; Switzerland [27]; Belgium and UK. The emission estimates for West Germany, Switzerland, UK [41] and The Netherlands [42], suggest that municipal waste incinerators and metal smelters/refiners are the largest sources of dioxin emissions to air. In Austria, domestic combustion of wood is believed to be the largest source followed by emissions from the metallurgical industry. Although an emissions inventory for Sweden has not yet been published [43], has identified emissions from ferrous and non-ferrous metals smelting/refining facilities as potentially the largest current source in Sweden. It should be noted that these emission inventories are expected to change over time due to changing industrial practices, facility closures and upgrades, and regulatory actions.

Some investigators have argued that national inventories such as this one may be underestimating emissions due to the possibility of unknown sources. This claim has been supported using mass balance analyses by various workers [44,45]. The Department of the Environment, UK [46] published a report on the quantity of dioxin released to land and water in UK. The main release sources were found to be; the production and use of some chemicals, the smelting of some non-ferrous scrap metals, the incineration of waste, and accidental fires. Pesticide use and production were found to be the largest sources of dioxin release to land and water. Other significant sources included the production of PVC and ethylene dichloride, electric arc furnaces [47], aluminium and lead recycling, municipal waste incineration, accidental fires, sewage sludge disposal and use of PCP and other biocides [48,49]. More detailed reviews of dioxins from MSW incineration and other fuel incineration systems will be presented in Section 5 of this review.

3. Toxic equivalent schemes

PCDD and PCDF congeners with chlorine atoms in the positions 2, 3, 7 and 8 are of particular environmental concern, especially the tetrachloro-CDD congener

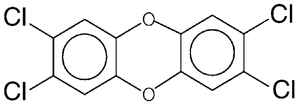

Fig. 2. Structural formula of 2,3,7,8-tetra CDD.

2,3,7,8-TCDD, which achieved notoriety following its release from the ICSEMA plant at Seveso, Italy in 1997. The structure of this target PCDD is shown in Fig. 2.

When establishing the toxicological effect of the dioxins present in the exhaust gases from an incineration plant, it is common practice to estimate a so-called “toxic equivalent” value based on the comparative toxicity of each dioxin congener/isomer present in the gas. This is due to the fact that although 2,3,7,8-TCDD is the most toxic of these compounds, it is generally present in much lower concentrations than the less toxic isomers. For this purpose, a number of equivalence models have been developed, the four most commonly adopted ones being presented in Table 3. All equivalence values are related to 2,3,7,8-TCDD which is a factor of unity. It can be readily observed from this table that the accepted relative toxicity levels for many of the isomers vary considerably from one model to another and that, in some models, non 2,3,7,8-isomers have been assigned a toxicity value. Consequently, this leads to significant inconsistencies from the use of such models.

The toxicity varies substantially among the different PCDDs and PCDFs. It is generally accepted that only 17 out of the 210 dioxin and dibenzofuran congeners are toxic. The congener with the greatest toxic potency, and for which the greatest amount of toxicological information is available, is 2,3,7,8-tetra-CDD.

Since 2,3,7,8-TCDD is the most toxic, and by convention is assigned a toxicity rating of 1.0 (called a toxic equivalent factor or TEF). The remaining 2,3,7,8-positional congeners are then assigned lower TEFs comparable to their toxicity, relative to that of 2,3,7,8-TCDD. The toxicity of any mixture of PCDDs and PCDFs, relative to 2,3,7,8-TCDD, can then be expressed by multiplying the concentrations of the 2,3,7,8-positional congeners present in the mixture by their respective TEFs. The resulting products for each congener are called toxic equivalents (TEQs), with units identical to that in which the concentrations of the individual congeners are expressed. The TEQ of the mixture is obtained by summing the individual TEQs.

Table 3
Equivalence factors for four standard models

Model name	NORDIC	USEPA	FRG UBA	EADON
2,3,7,8-Tetra CDF	0.1	0.1	0.1	0.33
Non 2,3,7,8-tetra CDF	0	0.001	0.01	0
2,3,7,8-Tetra CDD	1.0	1.0	1.0	1.0
Non 2,3,7,8-tetra CDD	0	0.001	0.01	0
1,2,3,7,8-Penta CDF	0.01	0.1	0.1	0.33
2,3,4,7,8-Penta CDF	0.5	0.1	0.1	0.33
Non 1,2,3,7,8-penta CDF	0	0.001	0.01	0
1,2,3,7,8-Penta CDD	0.5	0.5	0.1	1.0
Non 2,3,7,8-penta CDD	0	0.005	0.01	0
2,3,7,8-Hexa CDF	0.1	0.01	0.1	0.01
Non 2,3,7,8-hexa CDF	0	0.0001	0.01	0
2,3,7,8-Hexa CDD	0.1	0.04	0.1	0.03
Non 2,3,7,8-hexa CDD	0	0.0004	0.01	0
2,3,7,8-Hepta CDF	0.01	0.001	0.01	0
Non 2,3,7,8-hepta CDF	0	0.00001	0.001	0
1,2,3,4,6,8-Hepta CDD	0.01	0.001	0.01	0
Non 2,3,7,8-hepta CDD	0	0.00001	0.0001	0
OCDF	0.001	0	0.001	0
OCDD	0.001	0	0.001	0

While a number of toxicity rating schemes have been developed on a national basis, as shown by Table 3, the scheme that has been internationally adopted is that of NATCO/CCMS [50], under which the TEFs are termed international toxic equivalent factors, or I-TEFs [51]. The I-TEFs for the seventeen 2,3,7,8-positional congeners of PCDDs and PCDFs are presented in Table 4; all other congeners that may be present in a sample are assigned a TEF value of 0.0. The summation of individual TEQs for a mixture of OCDDs and PCDFs is termed the international toxic equivalent or I-TEQ of the mixture.

A recent revision of the TEF scheme was undertaken by the World Health Organisation [52]. The proposed scheme includes coplanar congeners of PCBs within the overall TEQ

Table 4
Toxic equivalent factors (I-TEFs)

Congener	I-TEFs	WHO TEFs
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	0.5	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.001	0.0001
2,3,7,8-TCDF	0.1	0.1
2,3,4,7,8-PeCDF	0.5	0.5
1,2,3,7,8-PeCDF	0.05	0.05
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.001	0.0001
Coplanar PCBs		
3,4,4′,5-TrCB	–	0.0001
3,3′,4,4′-TrCB	–	0.0001
3,3′,4,4′5-PeCB	–	0.1
3,3′,4,4′,5,5′-HxCB	–	0.01
2,3,3′,4,4′-PeCB		0.0001
2,3,4,4′,5′-PeCB	–	0.0005
2,3′,4,4′5-PeCB	–	0.0001
2′,3,4,4′,5-PeCB	–	0.0001
2,3,3′,4,4′,5-HxCB	–	0.0005
2,3,3′,4,4′,5′-HxCB	–	0.0005
2,3′,4,4′,5,5′-HxCB	–	0.00001
2,3,3′,4,4′,5,5′-HpCB	–	0.0001

scheme, by defining TEFs for 12 coplanar PCBs on the basis that their mode of action and the responses elicited in biological systems parallel those of the 2,3,7,8-positional PCDD/Fs. These are listed in Table 4 together with their proposed TEFs. The WHO–TEQ of the sample would be represented by the summation of the products of the concentrations of 17 PCDD/F congeners by their respective TEFs.

4. Health and intake aspects

4.1. Public concern and health implications of dioxins

As public awareness of environmental issues has developed so rapidly over the past 20 years, the group of compounds which causes the greatest concern is the dioxins, the generic name of PCDDs and PCDSFs. The presence, movement and behaviour of these compounds in air [53–58], in soil [59–65], and in the aquatic environment [57,66,67] has been studied extensively.

Public concern is aroused by the health implications of the dioxin family, particularly after the industrial accident at Seveso, Italy. Subsequent to this accident, there were significant increases in incidents of chloracne, liver dysfunction and other adverse effects in the surrounding area; this accident involved a short exposure to a very high dose of 2,3,7,8-TCDD, the most toxic dioxin congener.

USEPA [3] review classed 2,3,7,8-TCDD as a “probable” human carcinogen on the basis of mechanistic considerations, unequivocal animal carcinogenicity, and limited human evidence. This interpretation has been generally accepted by other regulatory agencies; for example, the UK government regards 2,3,7,8-TCDD as a “possible” human carcinogen. However, the USEPA’s assumption of a linear dose-response relationship at all dose levels has not been accepted outside of the US. All European regulatory agencies regard PCDDs and PCDFs as carcinogenic promoters and have defined a tolerable daily intake (TDI) based on a no observed adverse effect level (NOAEL) derived from animal studies. The World Health Organisation [68] classed 2,3,7,8-TCDD as a “known” human carcinogen, but continues to regard other PCDDs/PCDFs as “not classifiable” despite a similar mode of action to 2,3,7,8-TCDD.

4.2. Dose responses and tolerable daily intake levels

Other than carcinogenicity, the dioxins exhibit immunotoxicological, reproductive and developmental effects in mammals; for humans, the evidence is more uncertain [69–75]. The USEPA [3] recently reappraised their toxicity rating of PCDDs/PCDFs for 2,3,7,8-TCDD from the slope factor of 156,000 ($\mathrm{mg\,kg^{-1}}$ per day) to 100,000 ($\mathrm{mg\,kg^{-1}}$ per day)$^{-1}$. The approach adopted by the European regulatory agencies has been to assess chronic and acute animal studies for a full range of carcinogenic and acute animal studies for a full range of carcinogenic and non-carcinogenic effects based on NOAEL. European governments have developed a range of TDI, dosage levels. In 1996, the Health Council of The Netherlands reduced their TDI level from 4 pg, I-TEQ $\mathrm{kg^{-1}}$ bw per day to 1 pg I-TEQ $\mathrm{kg^{-1}}$ bw per day [76]. In Germany, safety factors of 1–10 pg I-TEQ $\mathrm{kg^{-1}}$ bw per day with the lower range considered as a precautionary TDI and the higher levels as a preventative TDI [77]. UK, France and Belguim adopted the WHO guideline of 1989, which made a recommendation of 10 pg I-TEQ $\mathrm{kg^{-1}}$ bw per day. Sweden, Norway and Finland have adopted a TDI level of 5 pg I-TEQ $\mathrm{kg^{-1}}$ bw per day based on using a NOAEL of 1000 pg I-TEQ $\mathrm{kg^{-1}}$ bw per day and a safety factor of 200.

In the UK, the Committee on Toxicology of Chemicals in Food, Consumer Products and the Environment [78] re-examined the existing UK TDI of 10 in relation to the USEPA report [3]. The UK COT considered the existing TDI was sufficient.

In 1998, WHO carried out a re-appraisal of their earlier TDI criteria for PCDDs/PCDFs [79] and adopted a range of 1–4 pg I-TEQ $\mathrm{kg^{-1}}$ bw per day, but instigating a review of the revised set of TEFs for PCDDs and PCDFs. These are discussed in Section 2 of the present paper.

There is extensive additional literature on the effects of PCDDs and PCDFs on humans and the general terrestrial and aquatic ecosystem. Several comprehensive reviews are also available (for example, [3,50,76,80–82]). The purpose of this section is to provide a summary of the physicochemical properties, environmental behaviour and toxic effects of these aspects to provide the background necessary for the design of MSW incineration system, in relation to the public perception.

In 1990, WHO acknowledged that the general population was already exposed to background concentrations of PCDDs and PCDFs approaching these stipulated intake ranges. Therefore, WHO recommended that all efforts should be made to reduce exposure to the lower end of their recommended range.

5. Dioxin emission limits

5.1. Current regulations on dioxin emissions

Over the last few years, controls over the release of dioxins to the atmosphere have become more widespread, with an increasing consensus in Europe for an emission limit of 0.1 nanogrammes per cubic meter based on the TEQ value ($0.1\,\mathrm{ng/m^3}$ TEQ). At the same time, the permitted emission levels for other pollutants have been significantly reduced (Table 5), with the result that possible areas of conflict could arise when alternative strategies are considered for dealing with the dioxin problem.

In UK, new limits on emissions of dioxin came into force on 1 December 1996 [83]. Under the 1989 EEC-directive on the incineration of municipal waste, MWIs in UK and Wales

Table 5
European regulatory emission criteria

	BPM 11/89 (mg/m^3, 15 °C 1 bar, wet)	TALuft 1990 (mg/m^3, standard dry, 11% O_2 (daily mean value))	EEC-directive (mg/m^3, standard dry, 11% O_2 (daily mean values))
HCl	100	10	5
$SO_x(SO_2)$		35	25
HF	5	1	1
$NO_x(NO_2)$		200	
CO		50	
Dust	50	10	5
Corg		10	5
Total acidity (SO_3)	750		
Total acidity (So_s)	5		
PCDD/PCDF (ng TEQ/m^3)	–	0.1	0.1
Total (ng/m^3)		1.0	

must comply with the new standards or cease operating. The dioxin emission limit has been set at 0.1 ng/m^3.

Based on the EEC dioxin directive of 1989, many central European countries [84] have adopted a permissible limit for PCDD/PCDF emissions from MWI plants. In Germany, the emission limit for PCDD/PCDF in stack gas of waste incinerators was set to 0.1 ng I-TEQ/Nm^3 by the 17th BimSchV. For industrial incinerators and thermal processes, a general minimisation rule was released with a guide value of 0.1 ng I-TEQ/Nm^3 for large-scale plants [85]. On the European level a few other countries, among them Sweden, Austria and The Netherlands, have also regulated the PCDD/PCDF emissions to 0.1 ng I-TEQ/Nm^3 for waste incinerators. In the US, a PCDD/PCDF emission limit for waste incinerators has only been released recently with the sum of tetra-through octachlorinated PCDD/PCDF set to 30 ng/Nm^3; the US emission limit is about five times higher than the valid German limit.

On 19 April 1996, EPA proposed revised emission standards for cement kilns and lightweight aggregate kilns burning hazardous waste [29]. These standards, including emission standards for CDD/CDF (0.20 ng TEQ/dscm at 7% O_2), were proposed under joint authority of the Clean Air Act (CAA) [86] and the Resources, Conservation and Recovery Act (RCRA).

5.2. USEPA regulations for dioxins in MSWI ash

On 19 December 1995, EPA promulgated CDD/CDF emission standards for all existing and new MSW incinerators (MSWIs) units with aggregate capacities to combust greater than 35 metric tons per day (Federal Register, 1995). The specific emission standards (expressed as ng/dscm of total CDD/CDF, based on standard dry gas corrected to 7% oxygen) are a function of the size, air pollution control device (APCD) configuration, and age of the facility as listed in Table 6.

Table 6
USEPA emission standards for PCDD/F in MSWI fly ash

1995 Emission standard (ng total CDD/CDF/dscm)	Facility age, size, and APCD
60	Existing: >225 metric ton per day; ESP based APCD
30	Existing: >225 metric ton per day; non-ESP based APCD
125	Existing: >35 to <225 metric ton per day
13	New: >35 metric ton per day

6. Dioxins from incineration processes

Emissions from incinerators are the flue gases, the fly ash and the slag. Technology advances in the past 15 years has decreased the levels of PCDDs and PCDFs in the fly ash and slag so dramatically, that they are difficult to measure. Furthermore, recent studies [87,88] have shown that secondary treatment of incinerator residues can reduce the dioxin levels by more than 99%.

During the burning of household wastes [89] dioxin levels of 1.2–5.4 μg/kg for an avid recycler and 0.75–0.90 μg/kg for a non-recycler system. Hospital waste incinerators have generally developed a poor reputation with emissions greater than 0.1 mg I-TEA/m^3 and in the past have emitted several hundred ng I-TEQ/m^3 [83].

Two different process technologies have been adopted for chemical waste incineration, namely, rotary kilns or thermal oxidizers [90]. The practice with rotary kilns is to burn the waste feedstock as a semi-solid with supplementary fuel. Dioxin emissions of 3 ng I-TEQ/m^3 and less were achievable, but when the emission limits were lowered to 0.1 ng I-TEQ/m^3, dry scrubbing had to be introduced to achieve the new guideline. Thermal oxidizers are conventionally used for incinerating liquid and gaseous chemical wastes. Very high combustion temperatures are normally used, around 1400 °C, but with correct operation, control and treatment systems; emission levels below 0.1 ng I-TEQ/m^3 are readily achievable.

Dioxin measurements taken at landfill fire sites are reported to be potentially quite high. Pilot tests for spontaneous landfill fires produced dioxin levels of 66–518 ng I-TEQ/m^3, but on a real study the values were 0.05–0.43 ng

I-TEQ/m^3 [91]. Several studies have been carried out utilising various fuels for house heating. Studies using coal combustion generated dioxin levels of 13.8–87.2 ng I-TEQ/m^3 [40]. Studies using lignite realised a value of 0.015 ng I-TEQ/m^3 and when salt was added the value rose to 0.109 ng I-TEQ/m^3 [92]. The analysis of soot from a wide range of wood burning stoves and ovens yielded dioxin levels in the range 549–6587 ng I-TEQ/kg [93]. Major interest and concern arises from the performance of MSW incinerators. In 1986, the World Health Organisation [94] reviewed the available data on PCDD and PCDF emissions from these facilities. From the correlation between dioxin levels and operating conditions, although complex, some useful conclusions could be made. It appeared that the dioxin range of compounds resulted from complex thermal reactions occurring from poor combustion or during the cooling cycle. The PCDDs and PCDFs were certainly destroyed after adequate residence times and temperatures above 800 °C [94,95]. In order to design MSW incineration systems to eliminate or minimise dioxin formation, it is important to understand how PCDD and PCDF formation takes place.

7. Formation of PCDD/PCDF in MSW incinerators

7.1. General

This section will discuss the thermal degradation of dioxin in incineration systems and then review the PCDD/F formation theories and factors affecting PCDD/F emissions. Particular attention will be given to precursors and also formation and reformation theory mechanisms downstream of the actual incinerator. These factors will be critical and provide the basis for the development of PCDD/F emission control strategies [47,96,97].

- Incomplete combustion of organic wastes in the combustion chamber leads to the formation of organic fragments, commonly termed products of incomplete combustion, and these can act as organic precursors to the dioxin/dibenzofuran molecule.
- The MSW waste components provide a source of chlorine, and of metals. The latter are incorporated into fly ash [98] which carries over to the cooler (250–400 °C) post-combustion zone of the incineration system.
- The organic precursors (potential dioxin forming compounds) adsorb onto the surface of the fly ash in the post-combustion zone, and following a complex series of reactions which are catalysed by metals (mainly copper) in the fly ash, leading to the formation of PCDD/PCDFs along with other chlorinated trace organics.

7.2. Destruction of dioxins and precursors in incinerators

Thermal degradation of dioxins is known to proceed very rapidly at the temperatures attainable in the flame zone of an incinerator. A study of the thermodynamics and kinetics of dioxin oxidation leads to the conclusion that there is no unique thermal or kinetic stability attributable to these compounds. In theory, oxidation is essentially complete, at temperatures above 500 °C although, in practice, it is generally agreed that combustion temperatures of 850 °C and a gas residence time of 2 s or 1000 °C and a gas residence time of 1 s are necessary for total destruction. Since decomposition increases exponentially with temperature and incineration temperature of 1200 °C, which is typical for chlorinated hydrocarbon wastes, requires a residence time measured in milliseconds for total destruction.

Attempts to correlate incineration temperature, CO concentrations and other indicators of efficient combustion conditions, with dioxin emission concentrations have been only partially successful. Poor, low-temperature combustion has been shown to result in relatively high emissions of dioxin formation. In an incineration chamber, non-homogeneous conditions may produce localised zones where low temperatures and sub-stoichiometric oxygen conditions can cause dioxin formation. These conditions are most likely to occur in solid waste incinerators such as rotary kilns, but can also occur in chemical waste incinerators due to poor atomisation of liquid waste, droplet impingement on the incinerator walls, etc. and/or insufficient turbulence within the chamber, resulting in poor mixing between liquid droplets and combustion air.

Three possibilities for the origin of PCDD/PCDF found in incinerator dust and stack gas have been considered. Firstly, the PCDD and PCDF are already present in the waste burned. Secondly, it is well documented that chlorinated aromatic precursors such as polychlorinated-phenols, benzenes and bi-phenyls act as “precursors” for dioxin formation downstream of the incineration chamber. Thirdly, the presence of active carbon provides the basic organic material and/or catalytic surface for catalytic surface for dioxin formation. The possibility of a homogeneous gas-phase reaction is also being assessed. To minimise these possibilities for dioxin formation, the optimum design of an incinerator must pay particular attention to the four cornerstones of high destruction efficiency–temperature, time, turbulence (mixing) and excess oxygen. In particular, the formation of carbons (soot) particles must be avoided because, once formed, there is likely to be insufficient residence time within the incinerator to achieve complete burnout.

7.3. PCDD/F formation and factors affecting emissions from combustion sources

The factors affecting emissions from combustion sources are the following:

1. PCDD in feed;
2. precursors in feed;
3. chlorine in feed;
4. combustion temperature;

5. residence time;
6. oxygen availability;
7. feed processing and
8. supplemental fuel.

The involvement of these factors during the formation of PCDDs is not well defined. Therefore, each of the factors is discussed separately.

7.3.1. PCDD in feed

PCDD/Fs enter the environment as contaminants of commercial products, such as wood preservatives and pesticides. The widespread use of these products increases the possibility of finding PCDDs in the feed of a combustion process. For example, PCP-treated wood may be used to fire boilers. Runoff may carry pesticide to water treatment facilities where the organics are incorporated into a sludge. The sludge may then be incinerated. Likewise, contaminated waste streams from manufacturing processes may be incinerated as an energy recovery procedure. One example is PCP sludge incinerators used at wood preserving facilities. If PCDDs are found in the feed of an inefficient or poorly controlled combustion process, it is very likely that they will be released to the atmosphere. However, suitable combustion conditions should destroy all PCCDs in any MSW feedstock and this source is no longer considered a primary route for the presence of dioxins in the dust and stack gas. Further evidence against the necessity of having PCDD/F, in the feedstock has been obtained. The burning of any organic material containing organochlorine compounds or even inorganic chlorides, such as sodium chloride [30] can generate dioxins.

7.3.2. Precursors in feed

Many hundreds of studies have focused on the formation of PCDDs and PCDFs from precursors. Many workers have presented detailed descriptions of the formation mechanisms of chlorinated CDDs from precursors [99–114]. This work organises CDD precursors into three classes.

Class I: polyhalogenated phenols, primarily with a halogen-*ortho* to the hydroxyl group, with a high probability of CDD formation [115,116].

Class II: *ortho*-halogenated phenols, primarily with a halogen-*ortho* to the hydroxyl group, with a high probability of CDD formation [117,118].

Class III: other chemicals having the possibility, but less likelihood, of CDD formation. These include chlorinated aromatic compounds [116,119].

The majority of the experimental work to date has centred on three classes of precursors: chlorinated phenols, chlorinated benzenes, and PCBs. PCDD formation from the combustion of chlorinated phenols has been tested extensively. Dechlorination of the highly chlorinated homologues can result in the formation of toxic TCDD isomers. Chlorinated phenols are used as wood preserves, herbicides, and sap stain control products. Wood or vegetation sprayed with chlorophenol may be disposed of by incineration or used as a supplemental fuel in boilers. In addition, chlorophenol, i.e. wastes, have the potential to be disposed of in sludge incinerators and industrial boilers.

Chlorobenzenes are used in solvents, dyes, pharmaceuticals and rubber production. These products make up much of the organic chlorine found in the feed of municipal waste incinerators. The associated waste products may also be disposed of in an incinerator or boiler.

Until 1975, PCBs were used as dielectric fluids in transformers and capacitors. PCBs have also been used in hydraulic fluids, plasticizers, and dyes. The low quality incineration of PCBs at waste disposal facilities or in boilers may result in PCDD and PCDF emissions.

7.3.3. Chlorine in feed

The chlorine content of fuel is obviously an important parameter affecting the formation of PCDDs or PCDFs. Shin and Chang [120] developed a ranked priority list of conventional combustion systems emitting polycyclic organic matter including OCDDs and PCDFs. The rationale presented for source ranking is based on fuel characteristics and combustion conditions. This work places great emphasis on both the chlorine content of the feed and the concentration of aromatics in the feed [104,121,122].

Other authors have demonstrated the effect of chlorine on PCDD emissions and it has been shown [40] that PCDDs were emitted from coal combustion only when chlorine was added and PCDD formation occurred during the combustion of pine in the presence of HCl, but no PCDDs were detected during the combustion of pine alone. Liberti et al. [123] studied the combustion of vegetables and found that when inorganic chlorine or PVC is added, PCDDs and PCDFs were detected in the ash. While the precursor theory has received widespread acceptance, these inorganic chlorine studies demonstrate that the specific mechanisms involved in PCDD formation are complex and not well understood. However, it can be generally stated that chlorine must be present for the formation of PCDD and general trends indicate that increased chlorine concentrations in the feed improve the possibilities of PCDD emissions. Although laboratory studies have indicated a correlation between chlorine input and dioxin emissions, no significant statistical correlation has been shown in field tests. Whatever effect chlorine has on stack gas PCDD/F concentrations in commercial scale systems, it is masked by other parameters such as particulates carry-over and the particulate matter filtration device temperature [124]. Therefore the role of chlorine is still uncertain.

Further studies [125–128] have shown the presence of sulphur dioxide reduces the level of PCDD/F formation during incineration processes. A number of mechanisms have been proposed but the basic concept is that sulphur [129] can scavenge the chlorine molecule in the presence of moisture producing SO_3 and HCl. An alternative mechanism [130] in that sulphur blocks the activity of metallic catalysts in the ash thus reducing their PCDD/F activity formation.

7.3.4. Combustion conditions

The remaining factors identified in the literature that affect PCDD emissions are combustion conditions. These include combustion temperature, residence time, supplemental fuel, fuel processing, and oxygen availability. Combustion efficiency is a function of all of these factors. In order to destroy PCDDs or prevent their formation, the combustion efficiency must be high. This requires a combination of high temperatures, available oxygen, high heating value fuel, and long residence times [131–134]. Even with these optimised combustion conditions end-of-pipe flue gas treatment is still required to meet PCDD/F emission limits of 0.1 ng/Nm^3.

7.3.5. Combustion temperatures

Experimental evidence suggests that temperatures of 500–800 °C promote PCDD formation, while temperatures greater than 900 °C destroy PCDDs. However, pyrolysis at temperatures greater than 700 °C causes 99% destruction of PCBs and no PCDF formation.

Combustion temperature is a function of the heating value of the fuel or supplemental fuel, the available air, and the degree of fuel or supplemental fuel, the available air, and the degree of fuel processing. Municipal waste incinerators are considered a major combustion source of PCDDs. The large mass burn units are characterised by low combustion temperatures. This is due in part to the high moisture, low heating value fuel, poor air/feed mixing as a result of a lack of feed processing, and lack of supplemental fuel. In comparison, many hazardous waste incinerators and high efficiency boilers are designed for efficient combustion. These units burn high heating value fuels or add high heating value supplemental fuels and, even if the air/fuel ratio is low, the air/fuel mixing is efficient. The fuel is processed to decrease moisture and improve mixing. In many cases, high temperature afterburners are used for the combustion of off-gases. Several studies have been identified that demonstrate the effects of high combustion temperatures on PCDDs and PCDD precursors. For example, no PCDDs were detected in the emissions of the Vulcanus incinerator ship during the combustion of PCDD contaminated herbicide orange. The combustion temperature during this study was 1600 °C.

7.3.6. Residence time

The residence time necessary to destroy PCDDs and the combustion temperature are inversely related. The higher the combustion temperature, the shorter the required residence time for PCDD destruction. Likewise, a low-temperature source will require a long residence time for destruction of PCDDs. Sakurai et al. [114] showed that an increase in both temperature and residence time decreased the formation of PCDDs from chlorophenol combustion. Similar results have been found at hazardous waste incinerators that run with 1.5–2.0 s residence times. Combustion sources with longer residence times and high temperatures are less likely to form products of incomplete combustion, such as PCDDs.

7.3.7. Oxygen availability

Oxygen availability is a function of both the air/fuel ratio and air/fuel mixing efficiency, both of which are of concern when burning solid fuels. Solid fuels and high viscosity liquid fuels such as waste tars burn as particulates or large droplets; therefore, portions of the fuel are burned in low oxygen or pyrolysis conditions. An insufficient supply of oxygen or poor air/fuel mixing will promote poor combustion conditions and PCDD formation. Insufficient air supply increases PCDD emissions from chlorophenol combustion. Municipal waste incinerators are usually fired with excess air. However, large mass burn units may have poor air/fuel mixing due to the lack of fuel processing or poorly designed air distribution systems. Activated carbon regeneration and wire reclamation incinerators are both designed to be operated with low excess air. All of these cases have been shown to emit PCDDs.

7.3.8. Feed processing

The feed material for a combustion source may be a liquid, a solid, or a gas. Both liquid and gas fuels can be easily mixed with air resulting in high combustion efficiency; solid feeds usually require some processing to improve combustion. Often solid feeds require drying, shredding, or separation to improve combustion. Similarly, high viscosity fuels (i.e. waste tars) require preparations such as preheating and atomisation prior to combustion.

Feed processing will determine in part both oxygen availability and residence time. Fine, homogenous feed particles will improve air/fuel mixing and combustion. Larger particles will require longer residence times and may result in local oxygen deficiencies due to poor mixing. High moisture will also decrease combustion efficiency. Therefore, highly processed homogenous feeds are less likely to emit products of incomplete combustion, such as PCDDs [119,135].

7.3.9. Supplemental fuel

When burning a low CV fuel, the addition of supplemental fuel will increase the combustion temperature and improve combustion. Hail et al. tested a boiler cofiring RDF with coal. The boiler temperature was 1200 °C, and no PCDDs were detected. Dow Chemical Corporation tested an industrial incinerator burning waste tars without supplemental fuel and found ppb levels of TCDDs in the fly ash. After the addition of a supplemental fuel, no TCDDs were detected.

7.4. Formation and reformation mechanisms and theories downstream of the incinerator

The presence of dioxins in the flue gases and on particulates in “efficient” combustion systems can be attributed to two possible formation mechanisms based on heterogeneous catalysed reactions.

- Dioxins are formed from precursors which are present within the fuel or waste, or which are formed during the combustion processes.
- De novo synthesis from non-chlorinated hydrocarbons, carbon, oxygen, chlorine and other atoms present in the combustion products.
- Some research work is being carried out on possible contributions to PCDD and PCDF formation from homogeneous reactions [136].

Post-incinerator dioxin formation may be due to reactions occurring on particles entrained in flue gas during the brief time they pass through the 300 °C zone, or from reactions on particles deposited on ductwork in the region where these temperatures prevail. Estimates of the activation energy for desorption of dioxin molecules from a particle surface suggest that, at temperatures below 400 °C, the rate of desorption of dioxin molecules from a particle surface is too slow for the observed dioxin concentrations to be produced during the transit time of the flue gas. If this is the case, then it may only be reactions on deposited particles that make a significant contribution to observed stack gas dioxin concentrations.

An alternative proposal is that, apart from possible gas-phase reactions, dioxins are formed under moderate temperatures in air from particulate organic carbon, by gas-solid reactions with oxygen and halides, influenced and activated by copper(II) [108]. It is claimed that the results from laboratory experiments clearly prove that particulate carbon is the primary source for dioxins. There is further evidence that carbon of different origins may serve as a source for the synthesis. The dioxin synthesis is catalysed by copper(II) chloride, but not by the chlorides of alkali, alkali earth Fe, Zn, Mn, Hg, Cd, Ni, Sn or Pb [137]. The optimum temperature for formation is 300–400 °C. The dioxin concentration obtained in the model experiments depend on reaction, time, concentration of particulate organic carbon, composition of the catalyst (chloride, copper) and of the atmosphere (oxygen, water). Based on this evidence it may be concluded that dioxin minimisation may be achieved in incineration processes by

- high burn-out of particulates, with low residual organic carbon and
- low residence time for particulates in the low-temperature zone (300–400 °C).

Although most chlorides do not appear to act as a catalyst during dioxin formation, they may provide a source of chlorine for the gas-solid reactions. In this case no chlorinated organic precursor material is necessary.

De novo synthesis of dioxins from particulate carbon is supported by experimental work showing the catalysed formation of dioxins from PCP results in yields several orders of magnitude greater than the de novo synthesis from particulate carbon, inorganic chlorides, and copper(II), under identical conditions of temperature, air flow rate and heating time [138]. This research did conclude, however, that particulate carbon can catalyse the formation of dioxins from PCP, and promote the dechlorination of highly chlorinated dioxins to lower congeners. There is still extensive debate over which of the mechanisms dominates, or whether both can participate. In the de novo synthesis the PCDDs/PCDFs form from a variety of carbon species, condensed to a polymeric network referred to as particulate carbon [95,100,110,121,139,140]. The precursor theory predicts PCDD/PCDF formation from chemical similar species such as chlorobenzenes and chlorophenols [101,104,106,111,113,133,141–147]. Other studies have extended studies of the precurser theory to two carbon chain length compounds such as ethylene and acetylene [148–153]. Other evidence for the precursor theory, from outside of the laboratory studies, has been obtained from estimates of the relative ratios of chloroaromatic compounds detected and measured in the flue stack gases of incinerators other than PCDD/PCDFs [133,154–156]. A detailed analysis of the de novo and precursor theory has been presented by Lenoir et al. [157] and these authors propose that the precursor theory is likely to be the dominant mechanism in MSW incineration.

The effects of hydrogen chloride on the formation of dioxins in combustion products from a burner firing on gas–oil, methane, propane, or ethylene have been studied in Belgium [158]. Hydrogen chloride was injected at concentrations up to 4.5% into the combustion gases from a domestic burner and experimental combustion chamber. Dioxins were always detected in the off-gases, and it can be assumed that de novo synthesis from the flue gas and HCl is a general phenomenon for all hydrocarbons. Furans were always more abundant than dioxins. The relationship between the HCl concentration and the general dioxin concentration under fixed combustion conditions appears to be exponential. In the reported tests dioxin formation was found over a temperature range from 900 to 240 °C.

Recently, it has been demonstrated [159,160] that polycyclic aromatic hydrocarbons also chlorinate and decouple to form PCDD/Fs. Since HCl is a combustion product of all organochlorine compounds, it follows that any of these compounds is a potential dioxin precursor on combustion. Furthermore, any industrial process where HCl is allowed to contact flue gases is a possible source of dioxins. If this direct contact cannot be avoided, the use of gas fuels or optimising the combustion towards low soot and CO levels, will minimise dioxin formation according to these results.

Laboratory studies on the effect of oxygen, carbon monoxide and hydrogen chloride show a weak correlation with PCDD/PCDF formation levels in MSW incineration systems [92,120,122,157,161]. It has been shown that chlorine was more reactive to chlorinate organic materials that hydrogen chloride [135,162,163]. The role of these compounds on PCDD/PCDF formation is still unclear as tests to correlate chlorine levels in the incinerator feed were unsuccessful during commercial sale system studies. In an MSW incineration system, it appears that PCDD/Fs are possibly formed in waste heat boiler/recover units and dust collectors [164–166].

The first aspect to consider is that the PCDD/F production may be related to the combustion conditions. Good combustion conditions in the incinerator with respect to time, temperature, turbulence and design, then the destruction efficiency will be high and the emission of PCDD/F at the exit of the incineration chamber should be safely low. However, PCDD/F may be produced at the flue gas passage if the flue gas contains unburned hydrocarbons, fly ash, and heavy metals; and the gas temperature is suitable for formation. Therefore, in assessing the potential for PCDD/F formation the combustion conditions must be considered.

7.4.1. Flue gas temperature

Although numerous studies were reported, the optimum formation temperature is still a controversial argument. Nevertheless, there is unanimous agreement that process temperature is the most influential parameter in dioxin formation [100,101,106,140,143,167–171]. The temperature effect on PCDD/F formation has been demonstrated by using various solid- and gas-phase reactants in various environments, and the reported optimum temperature spreads over from 300 to 500 °C.

Previous data from three research groups were analysed by Shin and Chang [120] and plotted as shown in Fig. 3 based on chlorophenol as a precursor. The experiments in the figure are the pioneering works in this area, of which research focuses were de novo synthesis with carbon in fly ash or model catalyst mixture. They did not concern gas-phase precursors and PCDD/F and analysed only the solid residue after the formation reaction. According to Altwicker [142], and Milligan and Altwicker [169], a major part of formed PCDD/F evaporates rather than remains in the solid phase at high temperatures above 350 °C, and this is why the detected optimum temperature in their experiments appeared to be 300 °C. Recent reports used reasonable solvents to extract the PCDD/F from flue gas and show the optimum temperature for PCDD/F formation to be higher than at least 300 °C except for Stieglitz et al. [121]. Milligan and Altwicker [169] showed that de novo synthesis in the existence of a chlorine source in the gas stream had a peak rate at 373 and 398 °C for PCDDs and PCDs, respectively.

However, most of the experiments in the figure did not consider the reaction of precursors such as chlorophenols, from which the formation rate of PCDD/F is 1 or 2 orders of magnitude higher than de novo synthesis. The maximum formation rate of de novo synthesis did not exceed over 200 ng min^{-1} (g of fly ash)$^{-1}$, while the reported formation rate by Milligan and Altwicker [169] at 150 μg/m^3 of chlorophenol the concentration was 3300 ng min^{-1} (g of fly ash)$^{-1}$. This is a reasonable value to account for the emission rate at real incinerators. The measurement studies of possible precursors in the flue gas showed significant amounts of chlorophenols, chlorobenzenes and polycyclic aromatic hydrocarbons. Hence, the formation from the precursor reaction must be considered to predict the formation rate correctly. All of the papers reporting the reaction of chlorphenol or other precursors showed the peak formation temperature of 400 °C. Milligan and Altwicker [169] showed that the total formation rate at low chlorophenol concentration conditions had a peak at 350 °C, but the rate at 400 °C was close to 350 °C and higher than 300 °C. As the concentration of chlorophenol increased, the peak formation temperature shifted toward 400 °C. They also showed that most of the PCDDs stayed in the gas phase at temperatures above 325 °C. Other studies [143,145,172] showed that the peak temperature of PCDD/F formation rate from the precursor reaction was 400 °C.

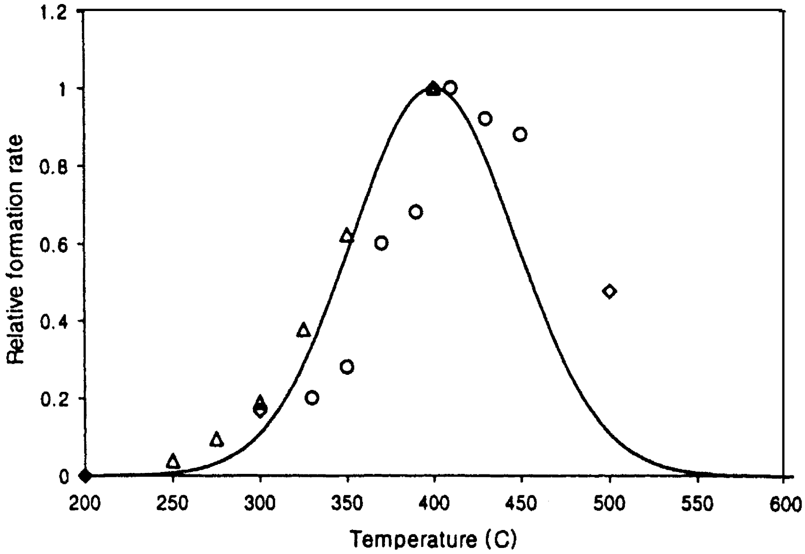

Fig. 3. Relative formation rates of PCDD/F (relative to 400 °C case): (∗) indicates data for the case of 700 mg/l of chlorophenol; (◇) [172]; (○) [102,143]; (△) [113,120].

Summarising, most of the experiments with a reasonable absorber for gas-phase PCDD/F show that de novo synthesis exhibits a peak temperature higher than 300 °C. The precursor reaction having a kinetic rate 1 or 2 orders of magnitude higher than de novo synthesis, appeared to have the peak formation temperature of 400 °C as the peak temperature of PCDD/F formation in an incineration system. Consequently, the temperature range of 250–450 °C in off-gas pre-treatment systems such as the electrostatic precipitator (ESP) or waste heat recovery boiler is adequate for the formation of PCDD/F. The presence of unburnt hydrocarbon may occur in the bottom ash, fly ash or flue gas, but it is likely to be present and is essential for PCDD/F formation. The largest source of unburnt hydrocarbon is usually attributed to the rapid volatilisation of hydrocarbons some of which pass out of the combustion chamber before being burned. The presence of dust and particulates is important. The dust emission rate has been shown to have a very close relationship with the PCDD/F emission rate. This has been attributed to unburnt carbon and/or metals in the particulates. The PCDD/PCDF ratios formed in MSW incineration systems have proved difficult to correlate [118]. The temperature seems to be the most important parameter but gas composition has also been stated as a possible explanation [103,107,111].

7.5. *Summary*

Extensive work by Shin and Chang [120] on 10MSWIs in Korea provides good information on the influence of system variables on PCDD/F formation which is supported by the previous discussion. The range of parameters to be considered include:

1. combustion temperature, control and conditions;
2. flue gas temperature profiles versus residence times;
3. ESP versus bag filters and
4. heat recovery boilers and water quenching (WS) spray drying absorber (SDA), ESP, bag filters (BF), dry injection of activated carbon (DIAC), activated carbon added to scrubbing solutions (ACSS), and selective catalytic reactors (SCR).

8. Dioxin minimisation during incineration

It is now possible to specify a set of operating condition guidelines which will lead to minimum formation of dioxins. These conditions should be considered only as guidelines for best operating practice and are discussed in the following sections.

8.1. *Precursor concentrations*

The presence of precursors in the feed in most instances is now not considered as a significant source of dioxin formation in a high temperature, highly effective combustion system. Although the presence of precursors such as the chlorophenols and chlorophenols is considered insignificant as a source of dioxins, they should be monitored periodically as sources of HCl and chlorine. However, the de novo synthesis of precursors could be as significant as their rate of formation is significantly greater that PCDD/PCDF formation from conventional de novo synthesis [97]. Several authors now support the formation of precursor compounds in the post combustion zone [150].

8.2. *Combustion temperature*

The major source for initiation of dioxin/furan formation is due to residues present from incomplete combustion. It is generally considered that at temperatures above 850 °C any dioxins/furans present in the feed will be destroyed, but for effective and complete combustion of particulate carbonaceous material a temperature greater than 1000 °C should be achieved.

8.3. *Residence time*

In addition to a high combustion temperature, it is recommended that a sufficient residence time should be allowed to ensure complete destruction of combustible material. At 1000 °C, a gas residence time in the combustion zone greater than 1 s is specified and at 850 °C a residence time of 2 s is recommended.

8.4. *Excess oxygen*

A further stipulation to ensure the complete destruction and combustion of any fuel particulates in the hot flue gas is the recommendation that a 3–6% (v/v) excess oxygen level is utilised.

8.5. *Turbulence in the combustion chamber*

Further efforts to ensure complete combustion can be made by creating turbulence in the combustion chamber. A Reynolds number greater than 10,000 is recommended and the most effective incineration furnaces have Reynolds number of 50,000 or greater.

8.6. *Computational fluid dynamic modelling in combustion system design*

The application of computational fluid dynamics has contribution significantly over the past few years and several design packages are available, such as ICE [173], CFD-AEA Technology [174], FLUENT [175], FACT [176], PCGC-3 [177], RICE [178] and KIVA [179]. In a major review of combustion models [180], the applications of CPD models for solving combustion reactions and mass, energy, momentum transfer equations were described. Several of the models and sub-models can be applied to describe temperature distributions, fuel particle volatilisation, char oxidation, radiant energy transport, gas compositions, particle trajectories, extent of particle burnout, NOX formation and reduction, SOX formation and removal, pressure distribution, particle size distributions and ash/slag accumulations. Premixed combustion modelling techniques were reviewed by Brewster et al. [181]. A major issue with MSW incineration and other fuel systems is effective turbulence. Cold spots are low-temperature zones in a furnace chamber where there is poor mixing or turbulence. These low-temperature zones result in poor combustion and the possibility of volatiles or unburnt particulate matter passing through the furnace, thus providing the components for de novo/precursor formation of dioxin in the cooling cycle. Comprehensive studies on turbulence modelling have been carried out by many authors [182–186].

The combustion models can provide significant assistance in the design of MSW incinerators, particularly in the area of turbulence, temperature distribution and particle burnout. However, the complex heterogeneous nature of MSW incinerator feed makes a detailed predictive analysis of gaseous products such as the chlorinated species impossible to predict within the current limits of knowledge, in particular, limited kinetic data.

8.7. Process instrumentation and control

Effective constant process conditions are required throughout the incineration process and these can best be achieved using automated process control. In particular, this includes providing a steady constant input of blended MSW. Interactive PCCS is normally used with interlock systems linked to on-line continuous gas monitoring and the monitoring of process parameters. Automatic waste feed cut-off is essential when these monitors indicate an upset process condition. In particular, effective control of the post-combustion conditions is essential [187]. Typical good control of these conditions for an MSW incinerator [188], are shown in Fig. 4.

Good combustion practice (GCP) coupled with pollution abatement equipment maintained in the region of 200 °C, will permit consistent achievement of PCDD/F emissions of 0.5–10 ng I-TEQ/m^3. Maintenance of GCP and operation of the pollution abatement equipment below 200 °C will help achieve further reductions to 0.1 ng I-TEQ/m^3 and below. Catalytic oxidation or treatment with activated carbon also enables emissions to be maintained below 0.1 ng I-TEQ/m^3.

The key control operating conditions pertaining to prevention of PCDD/F formation and minimisation of their release are as follows.

- Feedstock and feed control: attention to preparation of feedstock so as to avoid upset conditions within the combustor.
- Maximisation of combustion efficiency: adequate levels of temperature, residence time, supply of air (oxygen) and turbulence within the MSW furnace, so as to ensure efficient burn-out of the waste and minimisation of the formation of PICs.
- Management of waste heat boiler conditions: attention to

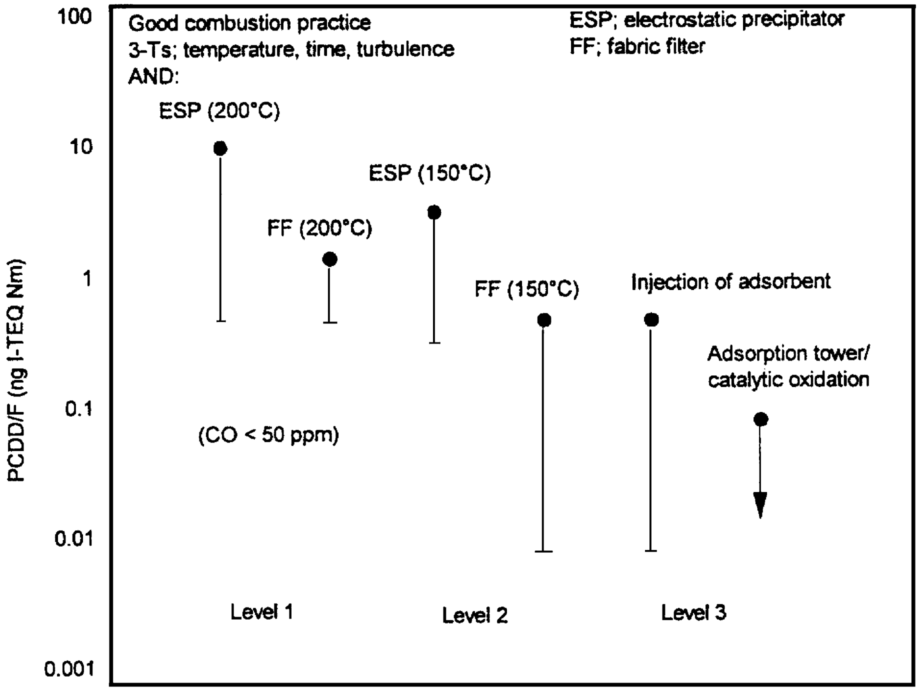

Fig. 4. Control of PCDD/Fs in MSW incinerators [181].

the cooling regime for combustion gases and minimisation of fly ash build-up.

- Management of pollution control devices: management of temperature regime and installation of appropriate PCDD/F removal processes.
- Control and monitoring of system variables: control and monitoring of critical parameters such as excess oxygen, CO levels, temperature, etc.
- Emergency and fail-safe systems: the provision of design and management measures that ensure the fail-safe response of the facility in the event of mal-operation or an emergency.

For most MSW incineration systems, the main emissions on-line control system is operated by immediate feed back from on-line measurements of carbon monoxide and hydrogen chloride in the flue gas at the stack control point. A high CO content in the flue gas will result in an increase in the combustion air flowrate into the incinerator. A high HCl level in the flue gas is indicative, but not confirmational, of potential dioxin formation and will result in the PCCS system processing in an increase in the active carbon/lime adsorbent dosage rate into the flue gas. Typically this is limited to ±20% change on the design value became above +20% change in adsorbent federate results in pipe blockages. Therefore if the HCl online detection system requires more than this +20% limit, the control system shuts down the MSW feed system and increases the feed of non-chloride/chlorine containing supplementary fuel.

8.8. *Critical temperature zone (CTZ)*

In the previous section, it was shown that several researchers have identified a critical temperature range or zone in which the rate of dioxin formation is at a maximum. Therefore the longer the combustion flue gases are allowed to remain in this temperature region the higher the level of dioxin/furan formation will occur. Until recently, the generally accepted CTZ is 350 to 250 °C, but there is still some discrepancy between the various sources of research data and a safe CTZ range is considered to be 400 to 180 °C. In Section 6, it was established that the CTZ for the maximum rate of PCDD/PCDF from precursors such as chlorophenol was 350–400 °C depending on the precursor concentration. Furthermore, the rate of PCDD/PCDF formation from these precursors is 1 or 2 orders of magnitude greater than dioxin formation rates from conventional de novo synthesis. The maximum rate of dioxin formation from de novo synthesis is in excess of 300 °C [113,134,139,143,148,172,189]. Therefore, in order to minimise dioxin/furan formation in this temperature zone it is necessary to cool the gases through the CTZ as rapidly as possible. The recommended process profiles is shown in Fig. 5.

Various techniques are available for rapid cooling of the gases from direct water injection to the relatively new process of semi-dry scrubbing (or spray drying) using a slurry of lime. The rapid cooling is achieved by evaporating the water in the slurry generating low grade steam. The disadvantage of this quenching process is the removal of valuable heat and the lowering of the energy efficiency cycle. Some heat can be recovered when the low grade steam is condensed, but the condensation temperature is considerably lower than the inlet hot flue gas temperature, therefore heat value is lost. However, two major advantages of the lime SDA quench process are (a) the rapid quenching in this temperature and (b) the lime absorbs/adsorbs hydrogen chlorine and chlorine forming calcium chloride, thus removing the hydrogen chloride sources in the CTZ, again minimising dioxin/furan formation potential.

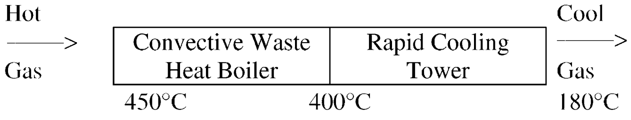

Fig. 5. Simplified key rapid cooling region.

8.9. *Precursor formation*

The early views on dioxin/furan formation consider the “precursor theory” as the main source of dioxins and furans. In more recent years, it was considered that precursors in the feed would now be destroyed in modern incinerators and the de novo synthesis became popular. However, in Section 7.4 it was apparent that many researchers now favour the theory of PCDD/PCDF formation from precursors, themselves formed after the incineration process, such as chlorophenols, chlorobenzenes and several other molecules. Consequently, any route leading to the formation of hydrogen chloride or unburnt or unsaturated ring systems could lead to dioxin/furan formation in the CTZ region. Therefore, there are a number of steps to ensure minimisation: (a) the chloride level in the MSW feed should be limited and controlled, this can be done both by periodic analysis of the feed or by monitoring chloride compounds in the flue gas outlet; (b) increasing the lime throughput in order to remove more chlorinated compounds, particularly hydrogen chloride. Furthermore, for optimum removal performance the SDA system is usually operated on a “once through” only system; this does produce additional material for disposal; (c) increasing the combustion temperature will lead to more effective destruction of hydrocarbons, thus minimising the quantity and type of unburnt hydrocarbons available for formation of dioxins/furans in the downstream processes; (d) activated carbon adsorption is used for final polishing to remove chlorinated compounds including furans and dioxins. Various types of carbon adsorbers can be used but the best performance is by using direct spray injection of powdered activated carbon. New processes based on photocatalytic destruction [190] are currently under investigation.

8.10. *Flue gas monitoring*

In order to ensure effective process control is being achieved and compliance is being attained monitoring is essential. Due to a combination of economics and legislative requirements a number of process sampling systems should be adopted. Continuous analysis of oxygen, SOX, NOX, hydrogen chloride, carbon monoxide and carbon dioxide should be implemented. Deviations from the specified criteria levels will indicate and upset process condition and will lead to an automatic shutdown of the MSW feedstock. This will be replaced by the conventional oil/gas supplementary firing fuel until stable conditions are re-established. In addition, monthly dioxin/furan samples and PCB levels should be taken for compliance analysis and weekly samples of Cl_2, HF and H_2S. Dioxin equivalence concentrations should be less than 0.1 ng I-TEQ/m^3. The dioxin/furan concentration should be less than the widely accepted environmental limit of 1 mg I-TEQ/g ash.

In most countries, MSW incinerators are required to have on-line continuous analysis of nine emission components. These are CO, CO_2, HCl, SO_2, NO_x, THC, particulates, water content, and O_2 on-line real time measurements. In addition, requirements are usually specified for off-line sampling dioxin, PCB, furan and heavy metals. Significant efforts are being made to develop an on-line analyser to measure dioxins or chemically-related precursors. The USEPA are supporting a project to search for compounds which are spectroscopically viable, are more abundant, and/or more easily detected such as precursors, chemically-related dioxins and furans which can serve as indicators of the presence of the full range of 2,3,7,8-chloro substituted compounds. The technique is based on resonance enhanced multiproton ionisation (REMPI) to detect proven precursors such as chlorophenols and chlorobenzenes [133], as well as indicators such as the mono- to tri-chlorinated dioxins and furans [191,192]. The technique is still in the development and testing stage.

8.11. *Turn down and start-up restrictions*

For best operating practice, MSW incinerators should not be fed with MSW during the start-up or shutdown operating cycles. A conventional coal, oil or gas co-combustion system should be utilised and the supplementary fuel should be used until the furnace structure has achieved its thermal capacity.

8.12. *Feed input preparation*

It is important to try to supply MSW feed, which is homogenous in texture, size, composition and which has been blended by shredding into a regular small sized feedstock. It is known that lumpy feed causes erratic combustion and generates unburnt material in the hot flue gases. Current thinking, that restricting chlorinated compounds in the feedstock is important, is now considered to be insignificant and high chlorine content feeds can be combusted effectively. However, the method of presentation of the feed to the incinerator is regarded as important.

8.13. *Optimum size of MSW incineration plant*

Small MSW incineration plants have difficulty in achieving combustion and are not very economic to operate. Very large individual incinerators can suffer from uneven temperature gradients, areas of poor feed distribution and localised cold spots, which support poor combustion and therefore are conducive to dioxin/furan formation. Based on the data in literature MSW incinerators operate most effectively and with minimum dioxins/furans formation in the range of throughputs from 350 to 400 ton/h. If a plant capacity needs to be larger, multiple units can be used.

8.14. *Air pollution control devices for MSW*

MSW incinerators are commonly equipped with one or more post-combustion APCDs to remove various pollutants to release from the tank (e.g. particulate matter, heavy metals, acid gases, and/or organic contaminants) [3,4,193–196]. These APCDs include:

- electrostatic precipitator (ESP);
- fabric filter (FF);
- dry scrubber (DS);
- dry sorbent injection (DSI);
- wet scrubber (WS);
- entrained flow adsorber;
- circulating fluidised bed;
- moving-bed adsorber and
- selective catalytic reactor.

8.14.1. *Electrostatic precipitator*

The ESP is generally used to collect and control particulate matter that evolves during MSW combustion, by introducing a strong electrical field in the flue gas stream, this, in turn, charges the particles entrained in the combustion gases [197]. Large collection plates receive an opposite charge to attract and collect the particles. PCDD/F formation can occur within the ESP at temperatures in the range of 150–300 °C. As temperatures at the inlet to the ESP increase from 150 to 300 °C, PCDD/F concentrations have been observed to increase by approximately a factor of two for each 30 °C increase in temperature [3,4]. As temperature increases beyond 300 °C, formation rates decline. Although ESPs in this temperature range efficiently remove most particulates and the associated PCDD/Fs, the formation that occurs can result in a net increase in PCDD/F emissions. This temperature related formation of PCDD/F within the ESP can be applied to distinguish hot-side ESPs from cold-side ESPs. For purposes of this categorisation ESPs are classified as follows:

- a cold-side ESP operates at or below 230 °C and
- a hot-side ESP operates at an inlet temperature greater than 230 °C.

8.14.2. *Fabric filters (FF)*

FFs are also particulate matter control devices, which remove dioxins associated with particles and any vapours that adsorb to the particles. Six to eight inch diameter bags, made from woven fibreglass material; are usually arranged in series. The porosity of the fabric allows the bags to acts as filter media and retain a broad range of particles sizes (i.e. down to less than 1 μm in diameter). The FF is sensitive to acid gas; therefore, it is usually operated in combination with spray dryer adsorption of acid gases.

8.14.3. *Dry scrubbers (DS)*

DSs, also called spray dryer adsorption, involve both the removal of acid gas and particulate matter from the post-combustion gases. By themselves, these units probably have little effect on dioxin emissions. In a typical DS system, hot combustion gases enter a scrubber reactor vessel. An atomised hydrated lime slurry (water plus lime) is injected into the reactor at a controlled velocity [197]. The hydrated lime slurry rapidly mixes with the combustion gases within the reactor. The water in the hydrated lime slurry quickly evaporates, and the heat of evaporation causes the combustion gas temperature to rapidly decrease. The neutralising capacity of hydrated lime reduces the combustion gas content of acid gas constituents (e.g. hydrogen chloride gas, and sulphur dioxide gas) by greater than 70%. A dry product, consisting of particulate matter and hydrated lime, settles to the bottom of the reactor vessel. The lime-water injection is usually in the range of 130–150 °C. DS technology is used in combination with ESPs or FFs. The DS reduced ESP inlet temperatures to make a cold-side ESP. DS/FFs have achieved greater than 95% reduction and control of PCDD/F in MSWI emissions (USEPA).

8.14.4. *Dry sorbent injection (DSI)*

DSI is used to reduce acid gas emissions. By themselves, these units probably have little effect on dioxin emissions. DSI involves the injection of dry hydrated lime or soda ash either directly into the combustion chamber or into the flue duct of the hot post-combustion gases. In either case, the reagent reacts with and neutralises the acid gas constituents [197]. A new system involves the use of activated carbon, sprayed into a dry/semi-dry scrubbing unit positioned after the particulate removal device and prior to the stack, has become a standard component in gas cleaning trains as a means of PCDD/F control, on all sizes or plant fed with MSW. Other adsorptive media such as zeolites are also being tested.

8.14.5. *Wet scrubber (WS)*

WS devices are designed for acid gas removal, and are more common to MSWI in Europe than in the United States. They should help reduce emissions of dioxin in both vapour and particle forms. WS devices consist of two-stage scrubbers. The first stage removes HCl, and the second stage removes SO_2 [197]. Water is used to remove the HCl, and caustic or hydrated lime is added to remove SO_2 from the combustion gases.

In addition to the APCDs described above, some less common types are also used in some MSWIs. An example is the electro-granular bed (EGB), which consists of a packed bed of activated carbon. An electric field is passed through the packed bed; particles entrained in the flue gases are given a negative charge, and the packed bed is given a positive charge. EGB systems function much like an ESP. Particulates matter is collected within the bed; therefore, EGB systems function much like an ESP. Particulate matter is collected within the bed; therefore, they will remove dioxins associated with collected particles and any vapour that adsorb to the particles. Only one facility in the US currently employs the EGB system, a fluidised bed-RDF MSWI. The effect of selected materials of construction of absorbers on the formation of PCDD/Fs has been studied [198–200].

8.14.6. *Entrained flow adsorber*

The device injects a powdered material into the flue gas duct and removes it downstream by fabric filter. The adsorbent (hearth-oven coke (HOC) or activated carbon as well as inertising materials or limestone) is recirculated as its sorption capacity is not exhausted after a single passage through the systems. The exhausted carbon-bearing adsorbent can be co-burnt in the combustion system.

8.14.7. *Circulating fluidised bed*

This process operates at a temperature of 100–120 °C and uses a fluidised bed adsorber downstream of the conventional flue gas cleaning equipment. The pre-cleaned flue gas is intimately mixed with fine-grained HOC and an additive, which aims to adsorb the dioxins. The dioxins loaded sorbent particles are removed in a downstream fabric filter and re-circulated to the fluidised bed adsorber. This process can also be used for simultaneous absorption of acid gases such as HCl, HF and SO_2 by suitable additives. The decisive advantage of the circulating fluidised bed over the entrained flow adsorber is the better utilisation of the sorbent due to the more favourable mass transfer conditions and longer solids retention times in the system.

8.14.8. *Moving-bed adsorber*

Fixed bed adsorbers [201] used for the flue gas cleaning have certain difficulties—blocking due to moisture absorption and corrosion. Therefore in flue gas cleaning plants, the fixed-bed adsorbers (using pure adsorbent) have meanwhile been largely replaced by the turbulent-contact method applied in moving-bed adsorbers with continuously exchanged adsorbent. After adsorption of dioxins the exhausted sorbents may be co-burnt in the combustion system, which must be equipped with suitable pollution control equipment. Alternatively, the exhausted sorbents are routed to an external disposal together with the fly ash from the upstream flue gas cleaning stages. According to new analytical results in the moving-bed technology special attention has to be paid to avoid the formation of the fine sorbent powder and in consequence, elevated dust-bound dioxin emissions on the stack.

8.14.9. *Afterburners*

Afterburners are often used for the incineration of unburnt components in the flue gases.

8.14.10. *Selective catalytic reduction*

It has been reported that catalysts employed for the selective catalytic reduction (SCR) of NO_x emissions also demonstrate the ability to decompose organohalogen compounds, including PCDD/Fs [202]. Successful pilot trials at MSW and hazardous waste incineration facilities indicated that PCDD/F emission concentrations of <0.1 ng I-TEQ/m^3 could be achieved in the absence of ammonia when titanium dioxide-based SCR catalysts were maintained between 200 and 350 °C.

8.14.11. *Control of particulate emissions*

As noted above, PCDD/F formation is via a surface-catalysed mechanism. It may therefore be thought that capture and removal of the particulate matter would necessarily result in a corresponding reduction in PCDD/F emission concentrations. If this logic were applied as a control strategy in isolation, it would suggest progressive lowering of particulate emissions as a simple means of PCDD/F emission control. Yet as a large number of studies have shown, it does not follow that a correlation between PCDD/F emissions and particulate emissions is necessarily observed in full-scale incinerators under all operating conditions. The reaction sequence is complex, and a number of variables affect the rate of formation and quantities of PCDD/Fs produced. For these reasons, particulate removal will not necessarily result in a proportional reduction in PCDD/F emissions. PCDD/F emissions can be controlled by means other than limiting particulate emissions (e.g. by controlling PCDD/F formation).

8.14.12. *End-of-pipe treatment*

The most effective of end-of-pipe treatment is the combination of a scrubber, a bag filter coupled with active carbon injection in the bag filter. Carbon consumption in this entrained flow process is around 50 mg/Nm^3. The bag filters should be operated below 200 °C, and preferably between 120 and 150 °C. The carbon can then be burned in the incinerator to destroy the PCDD/F and heavy volatilised metals will be removed in the scrubber. The performance characteristics of the three carbon systems are shown in Table 7.

Another effective technique is the use of SCR units or selective catalytic oxidation (SCO) units. Some SCR/SCO units work well, but some catalysts increase PCDD/F so care must be taken in catalyst selection. Also the gas temperature often needs to be increased, adding to energy costs.

8.15. *Ash management*

The incineration of MSW produces residual ash and flue gas containing PCDD/F [6,7,120,142,203–205]. Ash from MSWIs is required to be disposed in permitted landfills. In many countries, ash from MSEIs is not considered as an environmental release of PCDD/Fs and it is not included in such an inventory. In the USA, and estimated 7 million metric tons of total ash (bottom ash plus fly ash) was generated by MSWI ash samples for PCDDs and PCDFs. Ashes from five state-of-the-art facilities located in different regions of the United States were analysed for all 2,3,7,8-substitued PCDDs and PCDFs. The TEQ levels in the ash (fly ash mixed with bottom ash) ranged from 106 to 466 ng/kg, with a mean value of 258 ng/kg. PCDD/F levels in fly ash are generally much higher than in bottom ash. For example, Hutzinger and Fiedler [206] reported levels of 13,000 ng TEQ/kg in fly ash.

Each of the five facilities sampled in USEPA had companion ash disposal facilities equipped with leachate collection systems or some means of collecting leachate samples. Leachate samples were collected and analysed for each of these systems. Detectable levels were only found in the leachate at one facility (TEQ = 3 ng/l); the only

Table 7
Removal of PCDD/Fs from flue gases by the combination of scrubber, bag filter and activated carbon adsorption

Process	Equipment	Performance data
Entrained flow	Wet scrubber, bag filter with AC injection (trade name of AC: sorbalit) fabric filter ($T = 120$ °C) with AC injection (90% of the AC residues form the filter are re-circulated to the injection point)	PCDD/F in (a) untreated gas: 2.17 ng TEQ/Nm^3; (b) purified gas: 0.069 ng TEQ/Nm^3; removal: 96.8%; AC dosage: 50 mg/Nm^3; PCDD/F (a) before filter: 0.24 ng TEQ/Nm^3; (b) after filter: 0.01 ng TEQ/Nm^3; removal: 95.8%
Moving-bed	WKV/integral counter-current activated coke process (flue gas inlet temperature: 120–165 °C); moving-bed adsorber (flue gas inlet temperature: 150 °C; space velocity: 1000 h^{-1})	AC consumption: 500 ton per year per plant total gas flow: 464,000 Nm^3/h; PCDD/F stack emission: 0.015 ng TEQ/Nm^3; AC consumption: 5 mm of bed height per day; PCDD/F in (a) feed gas: 100 ng/Nm^3; removal: 98.8%
Fixed-bed	MEDISORBON/KOMBISORBON adsorber (a mixture of zeolit, 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 TEQ/Nm^3; (b) clean gas: 0.05 ng TEQ/Nm^3; removal: 83% (after 23,100 h test duration)

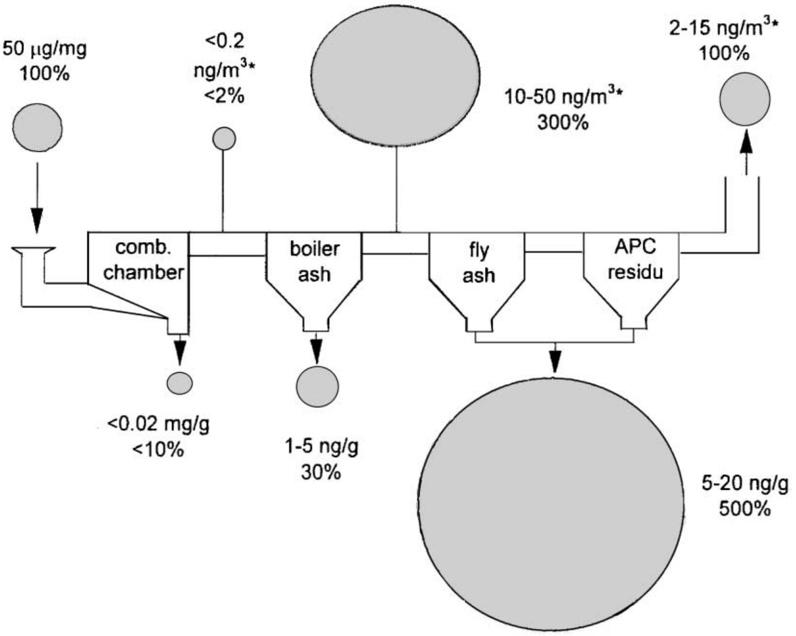

Fig. 6. Concentrations (TE) and balance of PCDD/PCDF in an old MSW incinerator: percent (%) is the proportion of total inventory input to the system; (∗) shows raw gas concentration.

detectable congeners were HpCDDs, OCDD and HpCDFs (see Table 1). PCDD/Fs are known to be only very slightly soluble in water.

In a Korean study [120], fly ash was sampled from eleven MSWIs and analysed for PCDD/F. Various levels of PCDD/F were found in the fly ash and there was a close linear correlation between the PCDD/F (ng/g) in the fly ash and the PCDD/F levels in the stack emission (mg/Nm^3). The amounts in fly ash varied from 8 to 2116 ng/g, from 0.13 to 21 ng I-TEQ/g. Therefore the factors affecting emission concentrations also affect the fly ash concentrations.

Heating fly ash from MSW incinerators in air at 300 °C results in an increase of PCDD/PCDF by de novo synthesis, catalysed by the fly ash [95,96,137,207]. The PCDD/PCDF formation from carbon particulates in MSW incinerator fly ash has been discussed as one potential mechanism for dioxin formation in the post combustion zone (250–450 °C) and with a long residence time, for example, in the ESP [100,168,208]. Significant research has been carried out into evaluating thermodynamic parameters for the de novo systems of PCDD/PCDF on incinerator fly ash [97,209–215].

As the design, management and control of waste incinerators has evolved over the past two decades, so the quality of ash produced by these facilities has improved with respect to PCDD/F content. A comparison has been shown in Fig. 6 representing old MSW incineration plant, and

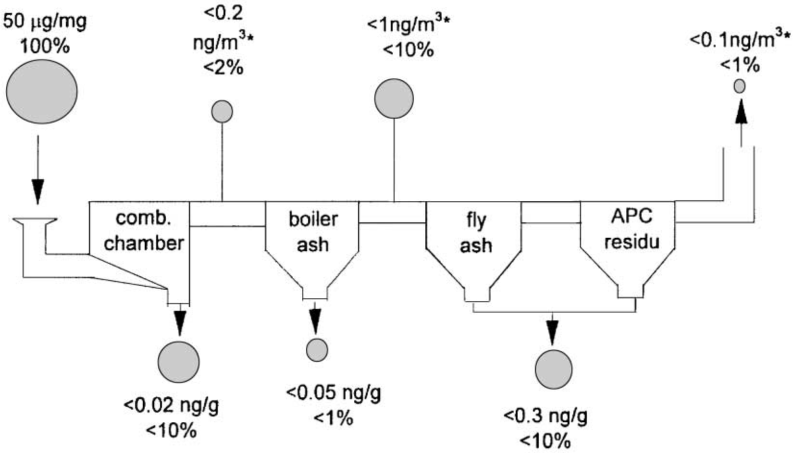

Fig. 7. Concentrations (TE) and balance of PCDD/PCDF in a modern MSW incinerator: percent (%) is the proportion of total inventory input to the system; (∗) shows raw gas concentration.

Fig. 7 representing modern facilities [216]. The former were potential net generators of PCDD/Fs relative to the quantity of these chemicals introduced into the incinerator via the waste feed. Consequently, PCDD/F levels could reach ≤20 μg I-TEQ/g in bottom ash from the incinerator grate, and 5–20 ng I-TEQ/g in fly ash from the pollution control device. However, modern well-operated plants are net destroyers of PCDD/Fs, with less of these chemicals existing in the facility via the stack, in wastewater and in solid residues than is introduced via the waste feed [217–219]. Consequently, PCDD/F levels in ash have reduced significantly, and are typically ≤0.02 ng I-TEQ/g in bottom ash, and less than 0.3 ng I-TEQ/g in fly ash from pollution control devices.

The expectations of PCDD/F concentrations in the ash from modern, well run incineration facilities should be well within the specified limit for ash quality, namely 1 ng I-TEQ/g. The proposed EU draft directive on waste incineration requires that the total organic carbon (TOC) content of the bottom ash be less than 3%, or their loss on ignition (LOI) less than 5% of the dry weight of the material.

Incinerator ash, and boiler ash and fly ash in particular, is a fine material that is susceptible to windblown dispersion if the material is not appropriately handled. MSW incinerators require standard ash management techniques, which include wetting of bottom ash and fly ash, collection of fly ash in hoppers connected to the boiler and fabric filter discharge points by airlocks, and stabilisation of the fly ash with cement-like materials.

9. Conclusions

The review has presented an introduction to dioxins, their characteristic properties and some physical properties. The paper presents the theories behind their formation and discusses the current controversies in this area. These relate to whether the principle causes of dioxins in MSW incineration are due to de novo synthesis between chlorine molecules and unburnt hydrocarbons sources present in particulates in the presence of certain catalysts or the de novo synthesis of well known dioxin precursors such as organochlorine compounds, chlorophenols, chlorobenzenes, etc. termed the precursor theory. Other critical process parameters which had significant impact on the dioxin formation potential of MSW incineration were also reviewed. This involved combustion temperature, turbulence in the combustion chamber, residence time in the combustion chamber, the post combustion flue gas temperature profile and the APCDs.

The key conclusions were that effective dioxin minimisation can be achieved by applying the following:

- combustion temperature >1000 °C;
- chamber turbulence Re >50,000;
- combustion residence time >2 s;
- post-combustion temperature: rapid quench cooling from 450 to 200 °C;
- air pollution control devices:
  - ○ semi-dry scrubber;
  - ○ bag-filter;
  - ○ activated carbon injection;
- process control: automated PCC system with interlocks and automatic MSW feed shut-off.

Following these process conditions will minimise PCDD/PCDF formation and lead to emission concentrations well below 0.1 ng I-TEQ/m^3.

Furthermore, due to the research on examining formation mechanism and field tests, the new regulations limiting dioxin emissions to 0.1 mg/Nm^3 means that MSW incinerator will no longer be significant sources of dioxins. The contribution of MSW incineration to the US dioxin inventory fell immensely in the period 1985–1995 [26]. Once all the US incinerators are in compliance in 2002, then the 1995 US dioxin inventory will drop another order of magnitude.

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