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Review

# The formation of dioxins in combustion systems

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## Abstract

Flame chemistry in incineration systems involves the formation of many organic products of incomplete combustion, including chlorinated species such as polychlorinated biphenyls (PCB), polychlorinated dibenzo-*p*-dioxins (PCDD), and polychlorinated dibenzofurans (PCDF). Because the latter are of environmental concern, a great deal of research has been expended on understanding their formation. There are two temperature windows in which they can form: the “homogeneous” route between 500 and 800 °C and the “heterogeneous” one at 200 to 400 °C. Homogeneous reactions, which are the result of the pyrolytic rearrangement of chlorinated precursors, such as chlorophenols and chlorobenzenes in the gas phase, have not been researched as extensively as the heterogeneous mechanism. Heterogeneous formation is a catalysed reaction, which takes place on the ash or soot particles present in combustion systems. There are conflicting views regarding the relative amounts of PCDD/F formed from precursors such as chlorophenols in comparison with the *de novo* process during commercial operations. The *de novo* reactions involve the oxidation and chlorination of any unburned carbon in the particulates. The reaction pathways for *de novo* PCDD/F are based on preexisting 3-ring carbon skeletons; single-ring chlorinated precursors are not intermediates. The formation process is driven by oxidation, and the rate is related to carbon burnoff. Dechlorination and decomposition proceed at elevated temperatures. The reaction appears to take place on the global (external) surface of the particles, but is determined by their carbon and chlorine contents. During *de novo* formation, chlorine is an active agent, either as chloride in the solid phase or as atomic chlorine in the gas. There is always a contribution from solid-phase chlorine, and gas-phase chlorine is active only at higher concentrations when the solid phase is depleted. An excess of chlorine appears to inhibit *de novo* formation. Different mechanisms are postulated for PCDD and PCDF. Single- and multiring species chlorinate differently, along different paths. The single-ring compounds formed are comparatively loosely held, while the multiring species tend to be strongly held. Much of the PCDD/F formed is retained on the solid surface and is unable to equilibrate with the gas phase under flue gas conditions. *De novo* catalysis is due mainly to copper, although iron and other metals are active at lower rates. Copper catalyses the oxidation of carbon, as well as the chlorination and dechlorination of organic products. In its two oxidation states it also acts as a “shuttle” for chlorine between gas and solid. The catalytic effect can be poisoned by sulfur or nitrogen compounds, such as sulfur dioxide and urea. All the formation models proposed to date both for the homo- and heterogeneous routes are inadequate, no doubt as a result of the complexity of the processes. The homogeneous route needs more fundamental research, and as regards the *de novo* route, more attention needs to be paid to the composition and nature of the ash’s surface, including particle size and carbon/catalyst disposition.

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### Nomenclature

Bz	benzene	MCP/MCDD/MCDF	monochlorophenol/ dibenzo- <i>p</i> -dioxin/dibenzofuran
CFD	computational fluid dynamics	MSW	municipal solid waste
CP	chlorophenol	OCDD/OCDF	octachlorodibenzo- <i>p</i> -dioxin/ dibenzofuran
DCP/DCDD/DCDF	dichlorophenol/ dibenzo- <i>p</i> -dioxin/dibenzofuran	P	phenol
DD/DF	dibenzo- <i>p</i> -dioxin/dibenzofuran	PCP/PCBz	polychlorinated phenol/benzene
ESP	electrostatic precipitator	PCDD/PCDF	polychlorinated dibenzo- <i>p</i> -dioxin/ dibenzofuran
FBC	fluidised bed combustor	PeCP/PeCDD/PeCDF	pentachlorophenol/ dibenzo- <i>p</i> -dioxin/dibenzofuran
GCMS	gas chromatograph/mass spectrometer	TCP/TCDD/TCDF	trichlorophenol/ dibenzo- <i>p</i> -dioxin/dibenzofuran
HxCDD/HxCDF	hexachlorodibenzo- <i>p</i> -dioxin/ dibenzofuran	TeCP/TeCDD/TeCDF	tetrachlorophenol/ dibenzo- <i>p</i> -dioxin/dibenzofuran
HCDD/HCDF	heptachlorodibenzo- <i>p</i> -dioxin/ dibenzofuran	USEPA	United States Environmental Protection Authority
ISI	iron and steel industry		
I-TEF, I-TEQ	International Toxicity Equivalence Factor/Quotient		

## 1. Introduction

The combustion of carbonaceous fuels results in the emission of the products of incomplete combustion, which include PCDD and PCDF (dioxins). The term dioxins is popularly used to describe a class of chlorinated compounds, which is correctly known as polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). The general structures of the 75 dioxin (PCDD) compounds and 135 furans (PCDFs) are given in Fig. 1. Some of these compounds are of environmental concern, as in a recent USEPA review they are implicated in damage to health [1], and 2378 TeCDD is classified as a “probable” carcinogen. Uncertainty surrounds the likely impact on humans, who are less susceptible to its carcinogenic action than rats [2], but who may suffer from endocrine disruption.

Various schemes for naming the compounds and their precursors are in use. The system of abbreviation used here for both precursors and PCDD/F is shown in the nomenclature, with the substitution positions designated as in Fig. 1. Toxicity is restricted to some of the congeners with 4 chlorine atoms or more in the molecule, with all having the 2378 positions occupied. As each is toxic to differing extents, a PCDD/F analysis is reported as its toxicity, generally based on International Toxic Equivalents I-TEQ ( $\text{ng N m}^{-3}$  for a gas sample and  $\text{ng g}^{-1}$  for a solid). The international toxicity equivalence factors (I-TEF) of the 17 active congeners are given in Table 1, relative to a value of 1.0 for the most toxic, i.e., 2378 tetrachlorodibenzo-*p*-dioxin (2378 TeCDD). The re-

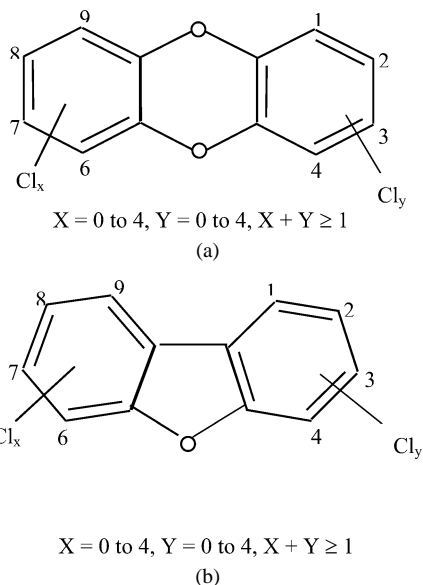


Fig. 1. Molecular structure of polychlorinated dibenzo-*p*-dioxins (a) and dibenzofurans (b).

mainder of the congeners are considered inactive, i.e., I-TEQ = 0. The current emission limit in Europe for municipal solid waste (MSW) incinerators is  $0.1 \text{ ng I-TEQ N m}^{-3}$ . The ratio of total PCDD/F mass to the mass of I-TEQ components ranged from 5 to 100 in the emissions from 17 different municipal and medical waste incinerators [3,4]. Shin et al. [5] give a mean value of 12 for MSW emissions from Korean incinerators. The figure depends on the distribution of

Table 1  
International Toxicity Equivalence Factors (I-TEFs) for PCDDs and PCDFs

CDD and CDF congeners	I-TEF
2378 Tetrachlorodibenzo- <i>p</i> -dioxin	1
2378 Tetrachlorodibenzofuran	0.1
12378 Pentachlorodibenzofuran (P)	0.05
23478 Pentachlorodibenzofuran	0.5
12378 Pentachlorodibenzo- <i>p</i> -dioxin	0.5–1 <sup>a</sup>
123478 Hexachlorodibenzofuran	0.1
123678 Hexachlorodibenzofuran	0.1
234678 Hexachlorodibenzofuran	0.1
123789 Hexachlorodibenzofuran	0.1
123478 Hexachlorodibenzo- <i>p</i> -dioxin	0.1
123678 Hexachlorodibenzo- <i>p</i> -dioxin	0.1
123789 Hexachlorodibenzo- <i>p</i> -dioxin	0.1
1234678 Heptachlorodibenzofuran	0.01
1234789 Heptachlorodibenzofuran	0.01
1234678 Heptachlorodibenzo- <i>p</i> -dioxins	0.01
Octachlorodibenzofuran	0.001
Octachlorodibenzo- <i>p</i> -dioxin	0.001

<sup>a</sup> The I-TEQ for 12378 pentachlorodibenzo-*p*-dioxin was upgraded from 0.5 to 1 by the World Health Organisation in 1997; equivalent to 2,3,7,8-TCDD.

congeners, which has been found to be relatively constant for MSW emissions. There is a predominance of furans over dioxins in these emissions, and the concentration of each group increases with the extent of chlorination. OCDF and OCDD are the most common congeners.

Using hierarchical cluster analysis, Fiedler et al. [6] examined the congener distributions of 109 emission gases from MSW incinerators, hazardous waste incinerators, and the iron and steel industry (ISI). The MSW and hazardous waste incinerators produce patterns that are indistinguishable. 23478-PeCDF is the most significant toxic congener in all three industries and contributes more than 30% of the I-TEQ. Recently, coplanar polychlorinated chlorobenzenes PCBs have been included into the toxicity considerations, as they appear to produce similar effects. Their I-TEFs are very low, except for 33'44'5 pentachlorobiphenyl, which has been allocated a value of 0.1 [7]. Also the bromo homologues of PCDD/F have been found to form more easily than the chloro derivatives, and bromine also appears to accelerate the concurrent formation of chloro compounds [8].

Because the concentrations present in flue gas are so low, and the full range of "dioxin" compounds must be quantified in order to establish an I-TEQ, the analysis of PCDD/F is difficult and expensive. A dedicated GCMS system of high resolution is required, and preliminary screening is carried out to remove interferences. Even so, an accuracy of only 50% in an individual sample can be expected under optimal con-

ditions [9]. Extreme care and cleanliness is required during sampling.

Originally, PCDD/F was thought to be totally of anthropogenic origin, beginning with the industrial revolution and associated with the large-scale use of chlorine compounds. However PCDD/F occur naturally and have been identified in Australian fluvial sediments laid down as early as 1640 [10]. The deposits are considered to be the result of volcanic activity or of bushfires in the surrounding countryside. Jüttner et al. [11] note other interesting natural occurrences. The estimated half-life of PCDD/F in natural sediments is greater than 100 years [12]. Nevertheless, the major input of PCDD/F into the environment is currently from industrial processes. PCDD/Fs are formed during pulp paper manufacture when bleaching is carried out with chlorine, and are by-products in the manufacture of some pesticides. The other principal source is combustion, such as waste incineration, including medical waste [13], iron ore sinter strands [14], electric arc furnaces using recycled steel [15], metal industries [16], landfill fires [17], and auto exhausts [18–20]. PCDD/Fs are not produced in detectable levels in cement kilns, even when firing chlorinated wastes. However, they can be released in the precalcining region under normal operation [21]. The wastes containing PCDD/F from paper making are discharged into the aqueous environment, while the sink for combustion products is in the atmosphere.

The anthropogenic release to the environment is estimated to have increased by 35 times between 1935 and 1970 [22], but recent figures suggest that these emissions are now decreasing [23]. A global mass balance shows an imbalance by a factor of 4 between estimated release and measured deposition fluxes, indicating that some sources are not accounted for [24]. The interaction of PCDD/F with the environment has been summarised by Alcock and Jones [25]. The stability of PCDD/F generated by combustion and adsorbed onto airborne particles has been studied in 25 m<sup>3</sup> outdoor chambers [26]. The PCDD/F formed at high temperatures (760–800 °C) were more stable to atmospheric photolysis than that formed at 350–380 °C. The lower chlorinated congeners were more susceptible to decay, with TCDD having a half-life of 0.4 h under summer conditions and 17 h in winter. The equivalent times for OCDD ranged from 5 to 38 h. Similar half-lives under ambient conditions are reported elsewhere [27].

A comprehensive survey of the gaseous organic emissions from incineration plants was carried out in Germany [28]. About 250 individual compounds were identified at concentrations above 50 ng N m<sup>-3</sup>, representing 42% of the total organic carbon emitted. The compounds included biphenyls, diphenyl ethers, dibenzyl dioxin, and dibenzofuran. The remaining

58% of the TOC consisted of unidentified aliphatic hydrocarbons.

The PCDD/F content of raw MSW is variable and ranges from 6 to 50 ng I-TEQ per kg of waste [29]. In early incinerators the output PCDD/F exceeded that fed in with the waste [30]. Recently a testing program in Spain involving a material balance for PCDD/F over a modern MSW incinerator showed that the system is approximately neutral, i.e., output  $\approx$  input [31]. The analyses indicate that the PCDD/F in the feed material is destroyed and then more is formed during processing. The bulk of the new PCDD/F is formed on the ash in the low-temperature back end of the incinerator [32]. In a pilot-scale fluidised bed combustor burning simulated MSW it was found that the ratio of high-temperature ( $\approx 900^\circ\text{C}$ ) to low-temperature ( $\approx 700^\circ\text{C}$ ) formation in the gas phase was dependent on the combustion zone's temperature, but was generally  $\approx 0.25$  [33].

This review addresses the formation of PCDD/F in high-temperature processes such as municipal and toxic waste combustion and metal processing. Previous reviews have been presented by Huang and Buekens [34] and Addink and Olie [35], who both reviewed formation in high-temperature processes. The latter summarises the formation experiments carried out in bench-top equipment up to 1995. Another by McKay [36], focuses on environmental effects and the minimisation of emissions from MSW incineration. The most recent review on formation chemistry (1998), by Tuppurainen et al. [30], examined the following aspects: (i) the influence of process parameters, (ii) the reaction mechanism, (iii) the form of reaction control, i.e., kinetic or thermodynamic, and (iv) whether laboratory experiments can simulate full-scale incinerators. The present paper concentrates on results which have appeared since that review, and updates their conclusions. Figure 2 is a stylised depiction of the paths by which chlorinated aromatic hydrocarbons form in combustion systems. The surface represents that of an ash particle and the arrows depict both reaction and adsorption processes. The thickness of the arrows represents the relative importance of the pathways in relation to PCDD/F formation, as proposed in this review.

## 2. The mechanism of PCDD/F formation in thermal systems

It is now apparent that trace quantities of PCDD/F can be formed under appropriate conditions in flames when carbon, hydrogen, and chlorine are present. Formation may be either in the vapour phase (homogeneous reaction), or on solid surfaces such as soot or ash particles (heterogeneous reaction). For both types

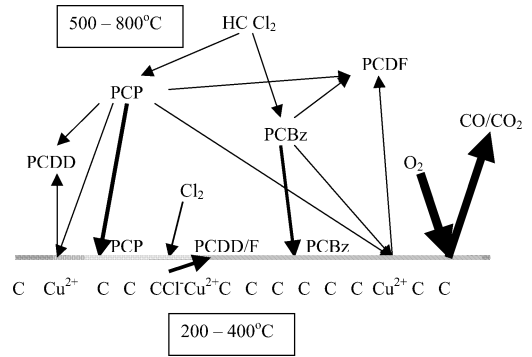


Fig. 2. Diagrammatic representation of the pathways for PCDD/F formation.

of reaction, the usual residence time of gas and solids in the critical temperature ranges of 800 to 500 °C (gas) and 400 to 200 °C (solid) is of the order of seconds. The PCDD/F emissions in stack gases depend strongly on the particle concentration, which is influenced by the extent of gas cleaning [37]. In a thermal system, the final result will be the difference between the rates of formation and thermal destruction. Since the activation energies of the destruction reactions are higher than those of the formation reactions, the net rate of production has maxima at certain temperatures for both the homo- and heterogeneous reactions.

The apparatus used for investigations into PCDD/F formation includes operating incinerators, pilot-scale combustors, and bench-top reactors. A technique used by the ISI to simulate sinter strands is the pot test, in which a bed of ore and  $\sim 4\%$  coke is packed into a container and then ignited from the top [38]. A stream of air is passed vertically upward through the bed so that a well-defined combustion zone moves downward through it. Results from all of these techniques will be discussed in the course of this review.

### 2.1. Homogeneous (gas-phase) reactions (500–800 °C)

A monograph by Choudry and Hutzing [39] discusses the range of possible pathways to PCDD/F from a chemist's point of view. The formation pathways of PCDD/F were examined in terms of classical chemistry by Ballschmiter et al. [40]. They identified four principal pathways with the distribution of products dictated by steric requirements and the available precursors:

1. the cyclization of polychlorobiphenyls
2. the cyclization of polychlorodiphenyl ethers
3. the chlorination of dibenzofuran
4. the dechlorination of OCDF.

All of these routes have been demonstrated in practice, as will be discussed later in the text. The probable reaction paths which produce either PCDD or PCDF are summarised by Karasek [41]. In a subsequent paper, Ballschmiter et al. [42] note that in a flame the principal radicals— $\cdot\text{H}$ ,  $\cdot\text{OH}$ ,  $\cdot\text{O}$ , and  $\cdot\text{O}_2\text{H}$ —can more readily extract an H atom than a Cl atom from an aromatic ring. Hence highly chlorinated benzenes and phenols are found in flue gases. In the incinerator flue gases sampled by them, the sum of 23 CP correlates (to a first approximation) with the sum of Te to HCDF, while the sum of 26 CP correlates with the sum of TeCDD to OCDD. They therefore identify more detailed pathways to PCDD/F via the formation of chlorobenzene radicals, and then chlorophenols.

Reactions which form PCDD/F in the vapour phase can involve suitable precursors at temperatures above  $500^\circ\text{C}$  (sometimes called pyrolytic formation or slow combustion). The precursors may be existing compounds such as PCBzs or PCPs, or may be formed by condensation from aliphatic hydrocarbons [43,44]. In general terms, it has been shown that homogeneously formed PCDD/Fs are related to precursors. The PCDD/F concentrations in flue gas from an MSW incinerator have been correlated with those of various possible precursor compounds [45]. For the furnace gases (exit temperature  $> 400^\circ\text{C}$ ) significant correlations were found ( $r^2 > 0.8$ ) with HeCBz, (PeCBz + HeCBz) and PCP. No cross-products were tested.

The concentration of PCDD/F in a flue gas stream will be determined by a balance between formation and destruction reactions [46]. The destruction reactions may represent straight pyrolysis or involve catalysed dechlorination and oxidation. Pyrolysis tests on these types of compounds suggest that they should be totally destroyed at temperatures above  $700^\circ\text{C}$ , but experimental results, e.g., from a pilot-scale FBC burning simulated MSW [33], indicate that they will persist at much higher temperatures. Procaccini et al. [47] examined the chlorination of low concentrations of benzene in a plug-flow reactor at cool-down temperatures of  $500$  to  $700^\circ\text{C}$ . Their results led them to suggest that Cl $\cdot$  radicals formed in a higher temperature zone persist in superequilibrium concentrations and attack trace level aromatics.

Weber and Hagenmaier [48] carried out gas-phase pyrolysis reactions on chlorophenols above  $340^\circ\text{C}$  and found that in the presence of oxygen both PCDD and PCDF were formed. They concluded that the first step is the formation of phenoxy radicals, which can then dimerize at the H-substituted *ortho* carbons. The displaced H atoms move to the phenolic oxygen. PCDDs are formed via *ortho*-phenoxyphenyl intermediates, and PCDFs via dihydroxybiphenyls.

The formation rates depend on the temperature, the substitution pattern of the chlorophenols, and the oxygen concentration. The dechlorination of OCDD by the hydrogen atom was studied theoretically by Fueno et al. [49] using density-functional theory. They found that the reaction was strongly exothermic ( $585\text{ kJ mol}^{-1}$ ), but had a low activation energy ( $38\text{ kJ mol}^{-1}$ ). The formation of a  $\sigma$ -complex is favoured at temperatures below  $600\text{ K}$  and chlorine abstraction above  $900\text{ K}$ .

High-temperature simulations in the laboratory have focused on the reactions of PCPs. DD, DF, and 1-MCDD were among the products formed by the high-temperature pyrolysis ( $300$  to  $1000^\circ\text{C}$ ) of 2 MCP in a flow reactor with a 2-s residence time [50]. Sidhu et al. [51] examined the formation of both the chloro and bromo forms of dioxin in a quartz flow reactor by means of the thermal decomposition of 246TCP and 246TBP in dry air. The residence time was 2 s, and the temperature range studied was  $300$  to  $800^\circ\text{C}$ . Care was taken to minimise wall effects. They found with 246TCP feed that a significant amount of product was present, mostly as 1268 and 1379TeCDD. The maximum conversion was 0.05% at  $600^\circ\text{C}$ , and diminished only slightly at a temperature of  $800^\circ\text{C}$ , as shown by the experimental points in Fig. 3. The brominated feed (246TBP) exhibited similar behaviour, but the conversion was  $\sim 500$  times higher than the chloro compound. The formation of furans from the three monochlorophenol (MCP) isomers under similar conditions has been studied by Yang et al. [52]. Dichlorodibenzofurans (DCDF) were the dominant furan product, with maximum formation rates at  $\sim 600^\circ\text{C}$ . The distribution of products suggests that they form by the *ortho-ortho'* condensation of the MCP to give *o-o'*-dihydroxybiphenyl,

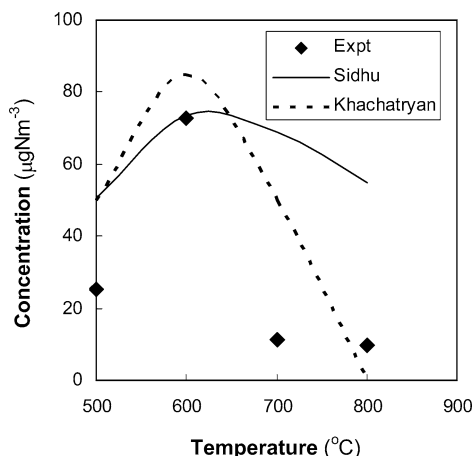


Fig. 3. Gaseous PCDD concentrations formed homogeneously from TCP after 2 s at various temperatures. (◆) Experiment [51]; (—) model [51]; (---) model [186].

which then loses H–O–H to form furans. Orbital calculations indicate that steric considerations determine the sites for subsequent chlorine substitution.

A similar set of experiments was performed by Nakahata and Mulholland [53] in a flow reactor with a residence time of 10 s, using a number of DCPs. Maximum formation of dioxins and furans occurred between 500 and 700 °C. Dioxins were formed by C–O coupling when *ortho* chlorines were present, whereas furans were formed by C–C coupling at unsubstituted *ortho* sites. With mixed DCPs, the TeCDF yields were greatest with phenoxy radicals having the least steric hindrance for C–C coupling. In all cases the formation of furan was favoured over dioxin from DCP containing one *ortho* Cl substituent. During combustion of polypropylene coated with a film of polyvinylidene chloride in a quartz flow reactor, it was found that significant quantities of PCDF were formed when the temperature of both the sample and the downstream gas was maintained at 700 °C [54]. After a 3-s gas residence time, 800 ng of PCDF was formed per gram of plastic burned, while PCDD formation was limited to 2.2 ng g<sup>-1</sup>. These amounts fell rapidly, when the reactor temperatures were increased.

A quartz flow reactor was used by Lujik et al. [55] with the purpose of investigating the precursor and de novo reactions over catalysed carbon. Some tests were carried out in the empty reactor at 300 and 600 °C to study the homogeneous condensation reaction of 246TCP. Very high ratios of PCDD to PCDF were observed, with the main products being 1368 and 1379TeCDD. The appearance of the more highly chlorinated dioxins (He and OCDD) is explained as further chlorination of the 246TCP by HCl released during the condensation of two of these molecules. The increase in temperature from 300 to 600 °C produces only a 10-fold increase in rates, which may be the result of wall effects, either catalysing the reaction at the lower temperature or destroying the products at the higher temperature.

The results from a test program on a mixed feed under controlled conditions undertaken by Marklund's group at Umeå university provide some of the most comprehensive data available [56–68]. The tests involved burning 5 kg h<sup>-1</sup> of artificial MSW in a pilot-scale fluidised bed. The flue gas was sampled at 650 °C at the exit of the bed freeboard before entry into a convection section, and then at 215 °C after passage through the convective cooler. The samples taken after the convector section contained 100 to 1000 times more PCBz, PCP, PCDD, and PCDF than those before the convector, and a greater proportion of higher chlorinated compounds. The concentration of PCDF in the gas before the convection section was 110 ng N m<sup>-3</sup>, with 45 ng N m<sup>-3</sup> of PCDD, which is typical of larger incinerators. The gas was rich

in unchlorinated dibenzofuran (20 µg N m<sup>-3</sup>), which had formed at temperatures above 650 °C. Most of this product appeared unchanged at the exit of the convection section. DCDF and DCBz form at low combustion efficiencies and higher homologues under good conditions. The primary formation of CDDs and CDFs is through different mechanisms. The CDDs are formed mainly from condensation of CPs, while CDFs are formed from a low or nonchlorinated precursor, followed by further chlorination.

## 2.2. Heterogeneous (solid-phase) reactions (200–400 °C)

When suitably catalysed, PCDD/Fs also form on solid surfaces at temperatures of 200 to 400 °C. They can form via two routes, either from precursors such as chlorophenols and chlorobenzenes [35], or from elemental carbon (the de novo reaction), see Fig. 2. The precursor molecules adsorb on the surface and react under the influence of metal catalysts to form PCDD/F. The de novo reaction is defined by Iino et al. [59] as the breakdown reaction of a carbon matrix, which may be residual in the ash, or soot. There is a rough linear relationship between stack emissions of PCDD/F from MSW incinerators and the concentration of flyash in the gas [60,61], indicating that the contribution from the solid phase predominates.

As with the homogeneous reaction, there is a good correlation between PCDD/F and other chlorinated products (and thus possible precursors). The concentrations of total PCBz in the flyashes from 11 MSW incinerators correlated with their PCDD/F contents [60]. In the FB combustor at Umeå burning simulated MSW, the concentrations of PCDD/F and PCBz on the flyash showed similar dependencies on temperature and residence time [62]. The maximum formation occurred at 340 °C and at the longest residence time (2.9 s). In a similar combustion situation, the total concentration of DCBz was proportional to the concentration of HCl [63].

The formation of chlorophenols during incineration, and their relationship to PCDD/F formation, was studied by Tupperainen et al. in a 50-kW pilot-scale incinerator [64]. During the combustion of doped fuel oil and RDF pellets, both the gas- and solid-phase flows were sampled. The distribution of PCPs in the product was dominated by species chlorinated in the *ortho-para* positions under the influence of the OH group. The PCDD/F distribution was typical of incinerators, with a PCDD:PCDF ratio of ~0.3. The results were analysed by partial least squares for statistical correlation. Different correlations between PCPs and PCDD/F were found for the gas and solid phases. In the gas phase, PCDF correlates closely with all PCP isomers, whereas on the solid the major correlations

are with 2346TeCP and 23456PeCP. In particular, the latter PCPs correlate with the Hx and HCDD/F congeners. The authors conclude [64] that the chlorophenols are either precursors or are formed and controlled by the same mechanisms and processes.

### 2.3. The interaction of PCDD/F with ash surfaces

The solids on which de novo reactions occur in incinerators or on iron sinter strands have been used to investigate heterogeneous reactions. However there has been remarkably little interest shown by researchers into the nature of the solids used in the experiments. Such properties as particle size distribution, surface area, and analyses for carbon, oxygen, chlorine, and metals are often not reported. The carbon content of a MSW flyash from a well-operated incinerator is usually in the range of 2 to 5% by mass. Those ashes used by Milligan and Altwicker [65] to measure oxidation kinetics contained 1.9, 2.0, and 7.4% carbon, and those by Hell et al. [66] 1.75 and 4.2%. The total organic carbon contents of two MSW flyashes are reported as 2080 and 1830 ppm or  $\mu\text{g g}^{-1}$  [67]. The organic chlorine content of one MSW ash was found to be  $\sim 400 \mu\text{g g}^{-1}$  [68]. The inorganic constituents such as Si, Al, Mg, Ca, K, Na, Mn, and Cr in a number of MSW ashes are listed by Cains et al. [69].

A number of particle sizes for individual analysis were screened by Stieglitz from a bulk sample of MSW incinerator ash containing 4.2 wt% carbon [70]. The carbon content increased in the larger particles, as given in Table 2, whereas chlorine is concentrated in the finer sizes. The carbon content of sinter strand ash taken from a precipitator was of the same magnitude for a comparable MSW ash particle size range [71]; see Table 2. The high chlorine concentrations of the samples from all sources should be noted. The PCDD/F contents of MSW ashes sampled from gas-cleaning devices can vary greatly, from 20 to 11,000  $\text{ng g}^{-1}$  of PCDD and 9 to 4400  $\text{ng g}^{-1}$  of

PCDF [28,72,73]. High concentrations are found with smaller particle sizes and in devices with long residence times, e.g., electrostatic precipitators. The congener distributions in typical MSW ash show increasing concentrations of PCDD homologues as chlorine substitution increases, but PCDF exhibits a peak in the Pe to H groups.

The precipitator ash taken from a sinter strand which was examined by Xhrouet et al. [71] contained 150  $\text{ng g}^{-1}$  of PCDD and 617  $\text{ng g}^{-1}$  of PCDF, which were equivalent to 1.7 and 15.1  $\text{ng g}^{-1}$  of I-TEQ, respectively. If a mean particle size of 40  $\mu\text{m}$  is taken for this ash, the surface concentration is similar to that for MSW ash (Table 2). The PCDD/F contents of ashes from three fields of an electrostatic precipitator on a sinter plant were examined by Buekens et al. [14]. The concentrations of PCDD in the sequential stages ranged from 0.4 to 29  $\text{ng g}^{-1}$ , and of PCDF from 1 to 84  $\text{ng g}^{-1}$ . The dust obtained from steel-making electric arc furnaces (EAF) may contain between 0.03 and 2.63  $\text{ng I-TEQ g}^{-1}$  [15].

The concentrations of PCDD/F for screened MSW fractions in Table 2 lie between 115 and 1217  $\text{ng g}^{-1}$ . The equivalent surface concentrations on an external basis can be estimated using the specific surface area  $S = 3/d_p$ , where  $d_p$  is the mean particle diameter in  $\mu\text{m}$  and a density of 2000  $\text{kg m}^{-3}$  is assumed. On this basis the surface concentrations were relatively constant, lying between 12 and 30  $\mu\text{g m}^{-2}$  [70]. Similar behaviour was found for PCBz and PCP.

In understanding the solid-phase reactions, it is important to quantify the rates of mass transfer, i.e., adsorption and desorption between the gas phase and the surface. The 17 toxic congeners have melting points in the range 196 to 305  $^{\circ}\text{C}$  and boiling points at atmospheric pressure between 438 and 537  $^{\circ}\text{C}$ . Their vapour pressures and the partition coefficients between solid and vapour determine the partitioning between the phases. Smolka and Schmidt [74] examined the partitioning of PCDD/F between gas and solid phases at low temperature in the flue gas from

Table 2  
Analyses of MSW and sinter flyashes

Sample	Size range ( $\mu\text{m}$ )	Elemental composition (mass%)				PCDD/F	
		C	Cl	Cu	Fe	$\text{ng g}^{-1}$	$\mu\text{g m}^{-2}$
MSW1	> 800	30.4	1.8	0.06	1.78	115	30.7
MSW2	300–150	5.2	4.5	0.11	2.79	170	12.5
MSW3	38–20	2.5	8.65	0.16	1.6	1217	12.2
MSW4	–	2.2	9.1	0.1	1.0	554	–
MSW5	–	1.1	4.5	–	–	–	–
Iron sinter	72.5% < 40 $\mu\text{m}$	3.3 (2.7) <sup>a</sup>	9.5	–	49.9	667	4.5

Sources: MSW 1–3 [70], MSW 4 [134], MSW 5 [72], iron sinter [71].

<sup>a</sup> As used in annealing tests after extraction.

two MSW incinerators. High volatile, i.e., less chlorinated, congeners were adsorbed comparatively more strongly than low volatile ones. In similar fashion it was found that PCDD/F and PC biphenyls were less strongly held on ambient vapour than PAHs and PC naphthalenes with similar vapour pressures [75].

Birat et al. [15] demonstrated that at low temperatures ( $< 100\text{ }^{\circ}\text{C}$ ) the congeners are physically condensed on the surface of EAF dust. Great affinity by PCDD/F for the ash surface of ESP dust taken from an iron ore sinter strand is reported by Wang et al. [76]. Mätzing et al. [77] carried out equilibration tests between flyash entrained in a gas stream and HCDD added as vapour. The residence time was 1.5 s and the temperature ranged from 25 to  $135\text{ }^{\circ}\text{C}$ . They report findings similar to those of Birat et al. [15], with the gas/particle partitioning at low temperatures corresponding to the sublimation equilibrium. At room temperature 90% of the added HCDD was found in the particulate phase, while at  $135\text{ }^{\circ}\text{C}$  the portion was only 10%.

Mätzing et al. found [77] that only about one-third of the PCDD/F originally present on a flyash could be removed by solvent extraction, leading them to conclude that the strongly bound material may not vaporise in their tests. It appears that significant amounts of PCDD/F are held on the surface of flyash particles, and do not participate in gas/solid partitioning. The more volatile PCDD/F components, e.g., TeCDF, are comparatively more strongly held (in relation to their vapour pressure) than the heavier molecules such as OCDF. The ratio of “bound” to free PCDF may be as high as 50 for TeCDF, and 5 for OCDF. Following some thermal tests on OCDF and OCDD adsorbed onto flyash, Collina et al. [78] concluded that some of this material is strongly held, and the remainder is weakly held. An estimate of the energy of adsorption indicates chemical bonding, even for the weakly held material. The fraction of the latter approaches unity above  $230\text{ }^{\circ}\text{C}$ , but no OCDD/F was lost into the vapour phase during tests at temperatures up to  $350\text{ }^{\circ}\text{C}$ . Hence they concluded that the material was all reacted into decomposition products. Tettamanti et al. [79] identified reversible adsorption/desorption reactions when the ash was heated in the  $50\text{--}300\text{ }^{\circ}\text{C}$  range under inert or oxidising gas. Irreversible exothermic reactions (carbon oxidation) appeared in the  $300\text{--}500\text{ }^{\circ}\text{C}$  range under air. When  $1234\text{TeCDD}$  was passed in the vapour phase with air over incinerator flyash [80], extensive, irreversible adsorption was found, with no breakdown to other congeners. As a result of this and other data, Stanmore concluded [70] that the extent of adsorption of PCDD/F onto solid ash from the gas phase is likely to be slight in incinerators.

The reactions involving precursors will involve their transport to the surface, coupled with various reaction steps on the surface, and any subsequent desorption of product. The activity of the surface is probably modified by species such as oxygen, water vapour, and sulfur dioxide. With the de novo reaction, the active agents are oxygen [80] and chlorine supplied from the solid itself and/or the gas phase [72]. It has also been reported that water modifies the rate of reaction [81,82]. Simulation experiments of PCDD/F formation should have residence times of the order of seconds, which necessitates the use of entrainment conditions. Unfortunately this approach has rarely been used. The bulk of the work has been done either in operating combustors where it is impossible to closely control conditions, or in fixed beds.

The continuous entrainment experiment of Gullett et al. [72] provides a good data set on formation, where the important variables were held at controlled values. The ash from an incinerator was conveyed in a gas flow through a reactor held at temperatures between  $250\text{--}400\text{ }^{\circ}\text{C}$  for periods of up to 5 s, with cooling under a controlled temperature gradient. Metered additions of oxygen, HCl, and chlorine were supplied. The ash loading was  $\sim 5\text{ g N m}^{-3}$ . In their experiment, Gullett et al. [72] found that the PCDD/F in the vapour phase was negligible in comparison to that extracted from the solid. Since the combustion of natural gas provided the flue gas well upstream from the point where flyash was added, the mechanism did not involve precursors in the gas phase, and negligible amounts of precursors were detected on the ash.

Addink et al. [83] found that all PCDD/F formed during annealing for 60 min at temperatures below  $348\text{ }^{\circ}\text{C}$  remained held on the particles surface. Desorption then commenced at higher temperatures, and at  $398\text{ }^{\circ}\text{C}$  between 75 and 98% of the PCDD and 47 and 92% of the PCDF had been lost to the gas phase. This represents higher temperatures for desorption than reported elsewhere. However, their PCDD/Fs were made from chlorophenol as precursor and the product from this reaction appears to be less firmly held than the de novo product. It has been proposed that PCDD/F found in the vapour phase forms on the flyash and then desorbs, but Stanmore argues that this is unlikely, because of the magnitude of the partition coefficients [70], and the competition for active sites with other adsorbents present at higher concentrations. One can conclude from the above and other evidence that de novo product is more strongly held than the precursor product, and a significant fraction is unable to participate in partitioning with the gas phase.



### 3. A survey of solid-phase formation

Most of the research on the solid-phase formation of PCDD/F on ash from MSW incinerators has been carried out in fixed beds, using both precursors and elemental carbon as the carbon source. The carbon may be either inherent unburned carbon or a material such as activated carbon added to an ash, which has been treated to remove inherent carbon. The ash is heated under an inert gas to the reaction temperature, and then either a precursor is passed as vapour through the bed of ash or oxygen is passed to promote *de novo* reactions. The tests are conducted over periods of 1/4 to 4 h. Stieglitz, who carried out many experiments of this kind, called the process “annealing.” For brevity, this name will be retained here.

Unfortunately, annealing experiments do not reproduce conditions in a real furnace. First the ashes are generally recovered from gas-cleaning devices and will be “aged.” There is a large difference between the rates measured in annealing laboratory tests and those measured *in situ* in furnaces, where residence times are typically of the order of seconds. These latter rates are measured when particulate samples are extracted directly from the gas stream in a duct or a stack. The exception to this is flyash collected in cleaning devices such as electrostatic precipitators and fabric filters, which may have residence times up to 30 min. A further complication is the possibility of a sampling artifact [84], when reaction continues between the sample gas stream and the ash deposit in the filter, as found with PAH. This possibility has not been definitively investigated [85]. The second difference is the absence of gas-phase chlorine, which means that the reactions are driven by oxygen-based reactions, with chlorine supplied from the solid matrix. Any influence of a chlorine supply from the gas phase is therefore eliminated. However, it has frequently been demonstrated, e.g., [86], that gas-phase chlorine (reported as HCl) has a significant influence on rate.

Lower temperature processes require catalytic action, which would implicate the contribution of non-gaseous phases, i.e., flyash surfaces. A comparison of the rates of formation by the precursor and *de novo* routes was made by Dickson et al. [87] in an annealing type of experiment. A feed of PeCP vapour in air was passed over a mixed bed of silica gel, anhydrous copper chloride, and powdered activated charcoal. The carbon of the PeCP contained  $^{13}\text{C}_6$  atoms, so that any product from this source could be identified. No mixed  $^{13}\text{C}_6$  $^{12}\text{C}_6$  molecules were detected in the experiments, which indicate that the pathways operated independently from one another. The formation rate from the PeCP precursor was of the order of 100 to 100,000 times faster than that by the *de novo*

mode under the same conditions. PeCP conversions as high as 55% are reported [87]. Surprisingly, high conversions were also found without the addition of the copper, which was interpreted as the catalytic effect of the carbon. Dickson et al. concluded [87] that the precursor route dominates the formation of PCDD/F in incinerators.

As a simulation of processes in an incinerator, these latter experiments can be criticised in several aspects, in addition to the general limitations of annealing experiments. Abnormally high concentrations of PCP were fed to the system, and complete contact of the precursor with the bed occurred over many seconds. In addition, flyash should have been employed, as it has been shown to be much more active for *de novo* formation than synthetic mixtures of the type used. This last criticism was accommodated when the above experiment was repeated with 2346TeCP and other chlorophenols, and a MSW flyash screened to < 210  $\mu\text{m}$  in size [88]. The Hx and HCDD/F in the product were assumed to originate from the precursor, and the remainder, which showed a similar pattern to previous *de novo* product, was assumed to result from the latter source. The precursor rate was up to 100 times faster than the *de novo* for 2346TeCP, but of the same magnitude for other chlorophenols. When the bed was diluted with inert glass beads, the result was strongly dependent on the ratio of gas-phase precursor to mass of flyash.

Although the formation rates from the two routes were comparable in the tests of Altwicker and Milligan [88], the concentration of PCP feed in the gas was far higher than found in incinerators. It is therefore unlikely that precursor formation is significant in practice. Huang and Buekens point out [89] that the ratio of PCCD to PCCF is always less than unity for *de novo* synthesis, whereas precursor reactions produce very little PCDF. From this and the fingerprint distribution of the congeners, they concluded that most PCDD/Fs from incinerators are formed via the *de novo* route. Addink et al. [90] came to a similar conclusion as Dickson et al. [87] regarding the dominance of the precursor route, but the question is far from settled. In the light of their modeling results, Huang and Buekens [89] suggest that because precursor concentrations are low, formation from precursors “plays no significant role in industrial incineration processes.” Typical precursor concentrations in a large MSW incinerator are  $3\ \mu\text{g N m}^{-3}$  for total chlorobenzenes, and  $20\ \mu\text{g N m}^{-3}$  for chlorophenols [28]. The situations where the precursor rates dominate may be where their concentrations are considerably higher than those quoted above, e.g., in systems starved of air, and in the pilot scale incinerator at Umeå [91].

Table 3  
Summary of recent precursor experiments

Solid	Catalyst	Gaseous reactants	Temperature (°C)	Comments	Ref.
MSW ash <sup>a</sup>	–	246 TCP, O <sub>2</sub>	250–400	TCP concn varied	[98]
Flor, KCl	CuCl <sub>2</sub>	246 TCP, O <sub>2</sub>	250–400	MSW ash more reactive	[98]
Flor, KCl	CuCl <sub>2</sub>	246 TCP, O <sub>2</sub>	250–400	Reaction order, kinetics, CO, CO <sub>2</sub>	[66]
MSW ash <sup>a</sup>	–	2346 TeCP, O <sub>2</sub>	250–400	Time and temperature varied	[176]
MSW ash <sup>a</sup>	–	2346 TeCP, O <sub>2</sub>	250–400	Adsorption measured, model	[93]
MSW ash <sup>a</sup>	–	2346 TeCP, O <sub>2</sub>	300	Comparison precursor: de novo	[88]
SiO <sub>2</sub> , C	CuCl <sub>2</sub>	PeCP, O <sub>2</sub>	250–350	Comparison precursor: de novo	[87]
MSW ash <sup>a</sup>	CuCl <sub>2</sub>	Organic, O <sub>2</sub> + HCl	348	Relative reactivities of organics	[90]
MSW ash <sup>a</sup>	–	PeCP	312	Comparison of 6 ashes	[69]
Borosilicate	CuCl <sub>2</sub>	C <sub>2</sub> H <sub>2</sub> , O <sub>2</sub> , HCl	150–400	HxCBz predominant product	[164]
Flor	CuCl <sub>2</sub>	PAH, O <sub>2</sub> + <sup>18</sup> O	250	High yield from biphenyl structure	[101]
MSW ash <sup>a</sup>	–	246 TCP, O <sub>2</sub> + H <sub>2</sub> O/HCl	150–500	<sup>13</sup> C in TCP	[105]
Al <sub>2</sub> O <sub>3</sub> , KCl	CuCl <sub>2</sub>	Bz, O <sub>2</sub>	400	<sup>13</sup> C in Bz	[104]
SiO <sub>2</sub>	CuCl <sub>2</sub>	DCPs	300–450	Major product 123468 HxCDD	[99]
Sand	–	DCBz, DCP, O <sub>2</sub>	585–390	Spouted bed reactor	[96]

In all cases the bulk of the gas feed was nitrogen. Flor is florasil, MgSiO<sub>3</sub>.

<sup>a</sup> Indicates a flyash extracted to remove organics.

### 3.1. Formation from precursors

In their review of mechanisms, Tupperainen et al. [30] proposed that the precursor route represents the major pathway to heterogeneous PCDD/Fs. The precursor reactions involving chlorophenols are effective between 200 and 400 °C, with a maximum around 300 °C [92,93]. Gullett et al. found a maximum at 400 °C when passing a mixture of 234, 235, and 236TCP over metal catalysts [94]. The yields were higher for the more highly chlorinated congeners. A summary of recent precursor experiments is presented in Table 3.

For PCDD/F formed from precursors over flyashes, Cains et al. [69] found that PCPs give only dioxin products and not furans. They concluded that PCDF forms via the condensation of unsubstituted phenol molecules, followed by chlorination of the dimer. Hell et al. [66] have reported tests with either 246TCP or 2346TeCP vapour over two MSW flyashes, held at constant temperatures between 250 and 400 °C. The main products are the oxides of carbon, but a range of chlorinated organic products, such as PCBz, and small amounts of PCDD/F were produced. With unchlorinated phenol as a precursor in the reaction with oxygen and free chlorine in the gas phase over CuCl<sub>2</sub>, the product PCDD contained little PCDF and the yield was independent of HCl concentration up to 100 ppm [90]. Between 100 and 200 ppm of HCl, a rapid increase in rate appeared. When three different commercial plastics were burned in a small furnace using metal chlorides for the Cl supply, the quantity of PCDD/F formed depended on the number of benzene rings present in the polymer [95].

A combustion experiment involving the oxidation of either 12DCBz or 24DCP in a fluidised bed was carried out by Ghorishi and Altwicker [96]. The bed was held at a fixed temperature, and the offgas was cooled to 390 °C. The levels of PCDD/F produced by the phenol were two orders of magnitude higher than by the benzene. Although the concentration of PCDD leaving the bed was much less than that of PCDF with a feed of 12DCBz, both increased rapidly (sixfold) in the cooling zone. The concentrations with 24DCP changed little. This should be compared with the Umeå pilot fluidised bed combustor, when operated on MSW with a with a 4-s residence time in the cooling system. It was found [57] that in the flue gas, the concentration of PCDF increased by a factor of ~30-fold during cooling from 650 to 215 °C. PCCD increased by ~15-fold. The results show that the distribution of congeners (i.e., the carbon skeletons) was relatively unchanged during cooling, and that the most prominent reaction was the chlorination of preformed species.

Luijk et al. [55] studied both precursor and de novo conditions over activated carbon and copper chloride in a fixed bed, using nitrogen or air as the gas. A preference for *meta* substitution on the carbon substrate was found. They claim that this preference reflects the formation of thermally stable precursors, such as 246TCP, 2346TeCP, and PeCP, which then condense to give mainly TeCDD and PeCDD molecules exhibiting *meta* substitution. This mechanism rules out formation by chlorination of the parent DD. The DD units are partially chlorinated in the matrix and then released when the surrounding carbon structure is burned off under the influence of

CuCl<sub>2</sub>. In contrast, the reluctance of classical aromatic structures to chlorinate in the *meta* position was demonstrated by Stieglitz et al. [97], who examined the polychlorobenzenes, polychloronaphthalenes, and polychlorobiphenyls formed under the same conditions as PCDD/F. The substitution in trichlorobenzenes showed a preference for the *ortho*-1,2,3 configuration, followed by the *para*-1,2,4 and only a small amount of *meta*-1,3,5. This may also be taken to indicate that there are separate formation pathways for the single ring and multi-ring compounds.

Similar experiments were performed by Addink et al. [90] on MSW flyash at 348 °C using chlorobenzenes, phenol, and larger aromatic molecules as precursors. Dihydroxyquinone gave a yield of PCDD/F which was 400 times greater than that of phenol, and 800 times greater than 1245TeCBz. PeCBz gave a negligible conversion. The authors concluded that quinine-type structures, and not chlorophenol or chlorobenzene structures, are intermediates in the formation of PCDD/F from carbon by the *de novo* process. They doubt that the *de novo* reactions are sufficiently rapid to contribute significantly to the PCDD/F content of fugitive ash.

A study of the conversion of 246TCP in a gas stream of 10% oxygen over two flyashes and a model flyash (SiO<sub>2</sub>/MgO mixed with KCl and CuCl<sub>2</sub>) was carried out by Hell et al. [66,98]. Most of the precursor was oxidised to CO and CO<sub>2</sub>, but between 2 and 25% was converted to PCDD/F. There is an optimum yield at ~300 °C, caused by competing formation and destruction reactions. Mulholland and Ryu [99] found a maximum yield at 375 °C when they reacted mixed PCPs over silica doped with 0.5% CuCl<sub>2</sub>. All the PCPs were chlorinated at the 26 positions and formed PCDD (not PCDF) at high conversion after 1 h of operation. There was a strong effect on the yield of the gas-flow rate, indicating mass-transfer control. The chlorination of dibenzofuran (DF) by disproportionation of CuCl<sub>2</sub> from 200 to 400 °C was studied by Ryu et al. [100]. They found that such chlorination was efficient in terms of copper usage, with MCDF always the dominant product. The maximum conversion to MCDF was at 225 °C and as the temperature was increased, the degree of chlorination increased. At 300 °C a maximum in the TeCDF congeners appeared, dominated by 2378 substitution. At higher temperatures broader distributions were observed, probably due to the destruction of 2378 congeners.

The behaviour during 250 °C annealing-type tests of PAHs with structures similar to DD and DF in the presence of silica/MgO (Fluorosil) and CuCl<sub>2</sub>·2H<sub>2</sub>O was examined by Wilhelm et al. [101]. The contribution of condensation products from PCBz and PCP can be neglected. Large amounts of PCDF were

formed from biphenyl, but no PCDD, leading to the conclusion that  $\alpha$ -hydrogen atoms were involved. Under the test conditions more than 72% of biphenyl was converted to PCDF, with a maximum amount of HxCDF produced. The result provides strong evidence for the intramolecular formation of the ether bond without further destruction of the reactant skeleton. Ethane and acetylene are also possible precursors, when passed over a silica/copper oxide bed in the presence of HCl in air [102]. A maximum in PCDF formation was found at 500 °C, and the congener patterns were similar to those formed over flyash. Heterogeneous combustion of C<sub>2</sub> aliphatics at temperatures above 600 °C was postulated as the route to chlorinated products. As a result of similar experiments with acetylene over borosilicate/CuCl<sub>2</sub>, Taylor et al. [43] proposed a condensation process which accounts for isomer distribution and branching, desorption of the higher molecular weight products, and regeneration of copper chloride catalyst.

The formation from anthracene and chloroanthracene was examined by Schoonenbaum and Olie [103], and an optimum formation rate appeared at ~300 °C. It was suggested that degradation products participate in the formation reactions. When the source of the oxygen-forming ether linkages was probed using <sup>18</sup>O<sub>2</sub> atmospheres and model flyashes doped with PAHs [104], very little incorporation of gaseous oxygen was found, except for HCDF. Charcoal in the mixture led to the inclusion of 30 to 40% of the oxygen in the product coming from the gas, when the PAH contained a carbonyl group. The authors speculated that H<sub>2</sub>O and Si-OH are other possible solid-state sources of oxygen. Analysis of the oxides of carbon evolved suggested different pathways for the oxygen found in the gaseous and solid products. An increase of ~50% in PCDD/F was reported when 30% of water vapour was added to the dry reaction gas in a system reacting 246TCP on flyash at 300 °C [105]. The further addition of 500 ppm of HCl gas suppressed the formation rate back to the value for the dry gas.

The hypothesis that the congener patterns are controlled by thermodynamic equilibrium was investigated by Addink et al. [106]. The congener distributions from various annealing experiments were compared to those predicted by a procedure, which minimised the Gibbs free energy of formation. Although the distribution of isomers within homologues was independent of reaction time, which suggests the attainment of equilibrium, there was poor agreement with the thermodynamic predictions. A discussion of the thermodynamic implications of proposed reaction mechanisms has been given by Tupperainen et al. [30]. The formation of PCDD is theoretically more favoured than PCDF, but the reverse is found in

Table 4  
Summary of recent de novo experiments

Solid	Catalyst	Gaseous reactants	Temperature (°C)	Comments	Ref.
Flor, KCl, C	CuCl <sub>2</sub>	O <sub>2</sub>	250–400	C <sup>12</sup> + C <sup>13</sup> in solid	[66]
MSW ash, <sup>b</sup> C	–	O <sub>2</sub> + H <sub>2</sub> O	300, 350	C <sup>12</sup> + C <sup>13</sup> in solid	[123]
Graphite	CuCl/CuO	O <sub>2</sub> + HCl	400	Hx, HCDF fingerprints like MSW ash	[109]
MSW ash <sup>a</sup>	–	O <sub>2</sub> + HCl, Cl <sub>2</sub>	235–375	Entrainment reactor, short times	[72]
MSW ash <sup>a</sup>	–	HCl, Cl <sub>2</sub>	250–600	Entrainment, solid-phase Cl significant	[111]
Al <sub>2</sub> (SiO <sub>3</sub> ) <sub>3</sub> , C, KCl	CuCl <sub>2</sub>	O <sub>2</sub>	300	Annealing 1 to 30 min	[114]
MSW ash, C	CuCl <sub>2</sub>	Inert, O <sub>2</sub>	300	Oxygen accelerates formation	[115]
Graphite	MCl	2.5% O <sub>2</sub>	300	MCl = KCl, CaCl <sub>2</sub> , FeCl <sub>3</sub> , CuCl <sub>2</sub>	[116]
Al <sub>2</sub> O <sub>3</sub> , C	CuCl <sub>2</sub>	O <sub>2</sub>	200–400	PCB product + 3467 PCDD/F	[117]
Flor, KCl, C	CuCl <sub>2</sub>	O <sub>2</sub>	250–400	C <sup>12</sup> + C <sup>13</sup> , PCP, PCBz measured	[92]
Carbon, MO	FeCl <sub>2</sub>	O <sub>2</sub>	275–325	MO = Al <sub>2</sub> O <sub>3</sub> , CaO, SiO <sub>2</sub>	[125]
MSW ash <sup>a,b</sup>	–	HCl, Cl <sub>2</sub>	240–600	Entrainment reactor	[137]
MSW ash <sup>a</sup>	–	O <sub>2</sub> + H <sub>2</sub> O,	250–600	Entrainment reactor,	[82]
		CO, CO <sub>2</sub> , Cl <sub>2</sub>		different routes to PCDD, PCDF	
MSW ash <sup>a</sup>	–	O <sub>2</sub>	300	Various hydrocarbon and Cl sources	[134]
MSW ash <sup>a</sup>	–	O <sub>2</sub>	250–550	NaCl active only if other Cl absent	[135]
MSW ash <sup>a</sup>	CuCl <sub>2</sub>	O <sub>2</sub>	300–350	<sup>37</sup> Cl used	[136]
Carbon + MO	FeCl <sub>2</sub>	O <sub>2</sub>	275–325	M = Ca, Al, Si, different carbon types	[128]
MSW <sup>a</sup> /Flor, C	CuCl <sub>2</sub>	O <sub>2</sub> + H <sub>2</sub> O	250–400	<sup>13</sup> C, different routes to PCDD, PCDF	[140]

In all cases the bulk of the gas feed was nitrogen. Flor is florasil, MgSiO<sub>3</sub>.

<sup>a</sup> Indicates a flyash extracted to remove organics.

<sup>b</sup> Indicates carbon removed.

practice. In a later paper [64], they suggest that *ortho-ortho* couplings should be favoured over oxygen-*ortho* couplings, thus favouring furans. Also the electron configuration of furans may confer stability by electron delocalisation, whereas the dioxin structure does not. The Ullmann reaction, which is the biaryl synthesis of chlorinated phenols, is likely at low temperatures (~300 °C), only if they occur via a C–Cl bond and not a C–H bond.

An analysis of the system's energetics has demonstrated the influence of the extent of chlorination on the free energy of reaction [106]. The thermodynamic study by Yuzawa et al. [107] predicted the equilibrium concentrations of the various congeners under typical conditions, with no PCDD/F formation likely above 360 °C. The influence of chlorine concentration on product distribution has also been considered from a free energy point of view [108]. In general, thermodynamic analysis yields little insight into the reactions.

### 3.2. De novo formation of PCDD/F

The mechanism of the de novo reaction is quite different from that responsible for formation from precursors. Early work by Stieglitz et al. [97] demonstrated the formation of other chlorinated organics from elemental carbon (charcoal), such as polychlorinated benzenes, naphthalenes, and biphenyls. The PCBz were formed in quantities 4 to 5 times greater

than PCDD/F over the same periods of time, but the other two products were present in lower amounts. A summary of recent experiments in de novo formation is presented in Table 4.

Iino et al. [109] found that the distribution of HxCDF and HCDF congeners formed from graphite with CuO and N<sub>2</sub>/O<sub>2</sub>/HCl at 400 °C for 2 h was similar to that extracted from flyash taken from the precipitator of an MSW incinerator. The fingerprint for PCDD/F produced during incineration generally shows a maximum in the PCDD spectrum at the Hx and H homologues, while the maximum concentration for PCDF is located at the Te and Pe homologues. The distributions of PCDD and PCDF among the homologues produced after annealing for 2 h are given in Fig. 4 in terms of temperature of formation [110]. At higher temperatures the dechlorination reaction favours the production of lower homologues.

The entrainment experiment of Gullett et al. [72] examined the variables: the concentrations of O<sub>2</sub>, HCl, and Cl<sub>2</sub>, temperature, quench rate, residence time, and the injection of Ca(OH)<sub>2</sub> as a sorbent. Formation rates of the same magnitude as found in operating incinerators were measured. It appears that the PCCD/F formed was the result of the de novo mechanism and took place in the temperature range 400 to 250 °C. Large amounts of PCDD/F were formed in the absence of gaseous HCl or Cl<sub>2</sub>, indicating that some of the 4.5% of chlorine in the solid was active in the reaction. Over 80% of the products under these

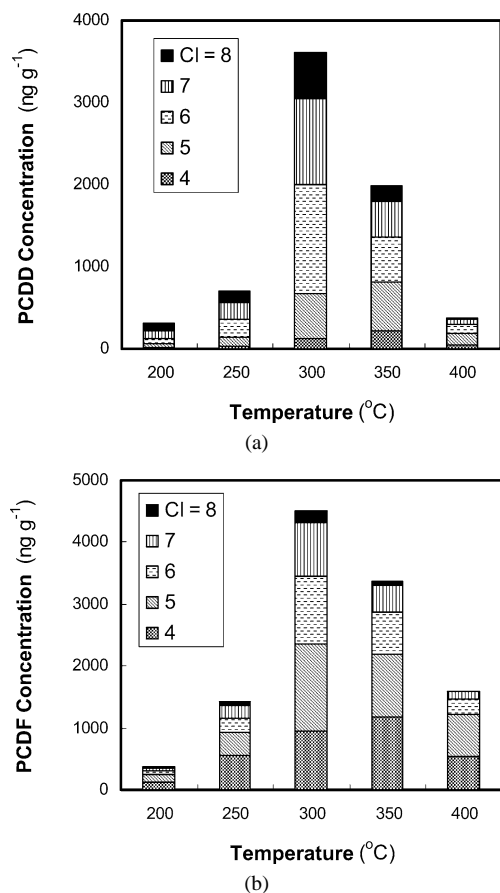


Fig. 4. Distribution of congener groups of PCDD and PCDF after annealing MSW ash for 2 h at different temperatures [110]. (a) PCDD, (b) PCDF.

conditions were furans. The most significant variables were found to be quench rate and sorbent injection, which reduced the concentrations of HCl and Cl<sub>2</sub>. The concentration of oxygen tended to influence the distribution of congeners more than the total quantity of PCDD/F formed. In a similar experiment by this group [111], the parameters investigated were the carbon content in the flyash, the reaction temperature and time, and the gas-phase composition (Cl<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O). The species CO and CO<sub>2</sub> were found to have no influence on the products. Water vapour slightly inhibited the formation PCDD/F, but significantly shifted the PCDF homologue profile toward the lower chlorinated congeners.

The mechanistic steps taking place during de novo formation are postulated by Gullett et al. [94] as:

1. production of Cl<sub>2</sub> from a metal-catalysed reaction of HCl and O<sub>2</sub>
2. chlorination of aromatic rings by Cl<sub>2</sub> through substitution reactions

3. formation of dual ring structures by a second metal-catalysed reaction.

Subsequent work seemed to indicate that the condensation of single-ring compounds is a minor route to PCDD/F formation. Jay and Stieglitz postulated [112] that during de novo formation PCDD/F forms from existing DF-type structures in the carbon matrix. The formation of de novo PCDD/F will now be considered in terms of reaction temperature/time and the supply of the constituent elements, carbon, chlorine, and oxygen, and finally particle size.

### 3.2.1. Temperature/time

There is a maximum in de novo formation of PCDD/F as a function of temperature as depicted in Fig. 4 during an experiment annealing MSW. The position of the maximum varies with the solid sample and the experimental conditions. For MSW in an entrainment reactor [111], the maximum amount of PCDD was produced at 300–400 °C, but most PCDF was generated at 400 to 500 °C. As the temperature increases, in most cases the ratio of PCDD to PCDF decreases. With increasing temperature, the fraction of less chlorinated homologues increases; i.e., the more highly chlorinated PCDF congeners appear to have been dechlorinated. Most studies, e.g., [110,113], have reported a maximum formation rate of PCDD/F between 300 and 350 °C, as demonstrated in Fig. 4. Very little has been found above 400 °C.

The only time-related data on PCDD/F formation currently available over a period of the order of seconds is from entrainment experiments, in which ash was fed to a downflow furnace [72,111], but time was not considered in detail. The influence of time was studied for the ash deposited on the furnace wall; over a period of 6 h the rate of formation fell continually. In a complementary experiment, a slug of ash was fed in 2 min and a gas-phase sample was subsequently taken. This gave even higher rates, but still would not simulate commercial furnace conditions. The shortest time period recorded during annealing experiments is 60 s [114]. The yields in most annealing tests were measured after comparatively long periods, for example, [97], after reaching a plateau. Data from the early stages are not recorded and extrapolation is impossible.

A steady increase in the amount of PCDD/F produced over times from 1 to 30 min was found during an annealing experiment (aluminum silicate/activated carbon/CuCl<sub>2</sub>/KCl) run at 300 °C [114]. Significant quantities were formed in the early stages (after 1 min there were ≈ 150 ng g<sup>-1</sup> of PCDD and 300 ng g<sup>-1</sup> of PCDF), similar to rates in industrial incinerators. The distribution of PCDD/F homologues, which remained constant over the test period, was classed as simi-

lar to that found from phenol precursors. The 1368 and 1379 isomers dominated the TeCDD, and 1236 and 1238 isomers the TeCDF. Since this is not typical of “thermal” formation, it was included [114] that chlorinated phenols play a key role as intermediates in the oxychlorination/degradation of carbon. The amount of PCBs formed remained constant over time, while PCPs and PCBzs steadily increased. During a similar annealing experiment on MSW flyash at 300 °C under extremely pure nitrogen [115], there was a steady increase in all congeners over a period of 3 h. When 10% oxygen was added, all the rates were an order of magnitude faster for about the first 10 min, but then fell or barely increased up to 60 min. After 3 h the yields had again increased significantly.

The results indicate that short-term de novo formation rates are extremely high, but fall with time and are orders of magnitude lower after some hours. This reflects a change in either the nature and reactivity of the carbon matrix or the inhibition of the metal catalyst. It reinforces the conclusion that measurements from annealing tests are generally unsuitable for describing reactions on ash entrained in combustion gases.

### 3.2.2. Carbon

During de novo annealing of flyash in air, the rate of release of PCDD/F is proportional to the rate of carbon consumption [68,116]. The chlorine is supplied from the solid. This is to be expected in the absence of gas-phase chlorine as the reaction removing carbon, and hence forming PCDD/F, will be driven by oxygen availability. The amount of PCDD/F produced during annealing at 300 °C was found to depend linearly on carbon content up to 4% C in ash and then showed no further increase [97]. A particular MSW ash was modified to give samples with varying amounts of carbon and then oxidised in entrained flow [111]. The three samples tested were as sampled (1.2% C), solvent extracted (1.0%), and oxidised to remove both organics and carbon (0.03%). There was an approximately linear correlation between the carbon content and the extent of formation of PCDD/F. Most carbon is lost as a mixture of CO and CO<sub>2</sub> and is not liberated as organic carbon such as PCDD/F [66]; see Fig. 2.

Schoonenboom et al. [117] have proposed a two-stage mechanism, whose first step is the chlorination of the carbon surface. The second is the oxidative decomposition of the chlorinated carbon to yield side-by-side 3467 or *meta*-chlorinated PCDDs and PCDFs. Since the chlorination is assumed to take place before the release of the PCDD/F product, the dominant chlorine configuration is not 2378 as dictated by considerations of electrophilic aromatic substitution, i.e., if there was a preference for *ortho* and *para* substitutions. The group of Stieglitz [68,92,97,118–122] in-

vestigated the mechanism of de novo formation by a program of annealing experiments. In one case an equimolar mixture of <sup>12</sup>C and <sup>13</sup>C (4%) with florisol to simulate flyash was used [122], with KCl added to provide chlorine and copper chloride as a catalyst. The products contained comparable amounts of bicyclic (dioxin) <sup>12</sup>C and <sup>13</sup>C compounds, but far less of mixed <sup>12</sup>C/<sup>13</sup>C compounds. Significantly greater amounts of furans were found, but virtually no mixed furan species were present. The yield of PeCBz increased with time, but that of PeCP showed no trend. Equal amounts of <sup>12</sup>C and <sup>13</sup>C PeCBz and <sup>12</sup>C and <sup>13</sup>C PeCP were formed. The authors concluded that 20 to 30% of the PCDDs are directly synthesised from single-ring condensations, but PCDF must be released directly from preformed multiring structures.

In a following paper, Hell et al. [92] found that the <sup>12</sup>C/<sup>13</sup>C fraction in PCDD does not change with reaction time. In addition, the <sup>12</sup>C/<sup>13</sup>C ratio in the other chloro products, such as PCP and PCBz, appears in the same ratio as in the carbon of the flyash. The work was further extended [118], with similar conclusions regarding the absence of mixed <sup>12</sup>C/<sup>13</sup>C products. The polychlorinated biphenyls formed are not produced from single-ring aromatics. They may act as precursors for the formation of PCDF, but not PCDD. The above results with tagged carbon and with tagged oxygen (see later) indicated that de novo PCDD/F is formed mostly from preexisting ring structures in the carbon skeleton, and rarely by condensation of the PCPs, which are simultaneously formed. One structure identified was the phenanthrene molecule, in which the central ring is displaced from the axis, i.e., has the “armchair” configuration. This was confirmed by Iino et al. [59], who used high molecular weight PAHs as the carbon source in annealing experiments. The frequency of formation of PCDD/F was proportional to the number of phenanthrene skeletons at the edges of the molecules. The 5-ring perylene structure was also identified by Weber et al. [123] as a likely source structure in the carbon matrix.

When graphite was used as the carbon source in annealing experiments under 10% oxygen at 400 °C, it was found [109] that the congener patterns were similar to those produced in incinerators. The distributions for HeCDF and HCDF were similar for three different tests: graphite +5% CuCl<sub>2</sub>; graphite + CuO + 500 ppm HCl; and straight flyash. Approximately equal amounts of product were present in the gas and solid phases, except when HCl was added. The type of carbon used influences the amount of product: graphite < soot < carbonised glucose < charcoal [124]. The rates in similar experiments using three halides in mixtures of flyash + charcoal + CuSO<sub>4</sub> + NaX were the same as for chlorine. If extra chlorine is available from the gas phase, the rate of

PCDD/F formation may be enhanced, but can only be released while the carbon matrix is being destroyed. Experiments tracing the formation of CPs as a function of the carbon content of the feed to the microreactor produced only a weak correlation.

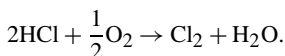
Ryan and Altwickler [125] tested five different carbons in oxygen-free annealing experiments catalysed by ferrous chloride. The  $\text{FeCl}_2$  acted as both a catalyst and a chlorinating agent. Of the carbons, activated carbon was the most reactive, but gave only 1.85 times more PCDD/F than graphitic carbon. The two carbon blacks tested had bulk densities of 680 and 350  $\text{kg m}^{-3}$ . They displayed different reactivities when calculated on a mass basis, but similar values on a carbon volume basis. As the spherule sizes of the carbons were similar, this suggests that global surface area is the significant variable. The influence of carbon surface area on the products from annealing has been considered by Stieglitz et al. [121]. Although the specific areas of the carbons tested ranged from 22 to 1090  $\text{m}^2 \text{g}^{-1}$ , as measured by the BET technique, they had only a minor influence on the yield. Accordingly, solid-solid reactions were considered to be the rate-determining step, rather than the reaction of oxygen with solid carbon. This has significance for any attempt to model the reaction.

### 3.2.3. Chlorine

Chlorine may be supplied from a solid, e.g., by the decomposition of a metal chloride, or by the chlorinated products of incomplete combustion, or the chlorine present in the gas phase. In the latter case, chlorine exists as atomic Cl, molecular  $\text{Cl}_2$ , and HCl. Gullett et al. [126] have discussed the effect of chlorine in detail, and have concluded that atomic Cl is the active species in the gas phase. Its concentration is determined by the combustion conditions: extensive formation of free Cl atoms from HCl and  $\text{Cl}_2$  is possible at high temperatures, and high concentrations may remain at lower temperatures after rapid quenching, because of kinetic constraints.

Copper acts not only as a catalyst but also as a transmitter of heterogeneous chlorine. When present in excess as  $\text{CuCl}_2$  with MSW ash, it was able to chlorinate activated carbon through to chlorinated benzenes and PCDD/F at 300 °C [112]. In the solid phase, the thermal decomposition of  $\text{CuCl}_2$  has been studied at temperatures from 300 to 400 °C [127]. At 300 °C under inert conditions, no disproportionation to  $\text{Cu}^{\text{I}}$  and free chlorine was observed, but the addition of oxygen brought about the reduction of  $\text{Cu}^{\text{II}}$  to  $\text{Cu}^{\text{I}}$ . At 400 °C extensive disproportionation occurred. This suggests that the copper acts not only as a catalyst for condensation, dechlorination, etc., but also as a shuttle for chlorine between the gas phase and the solid carbonaceous material. After donating

Cl for chlorination of the organic material, the  $\text{Cu}^{\text{I}}\text{Cl}$  residue is rechlorinated by gas-phase chlorine species. The chlorination of organics may involve the release of free chlorine by the Deacon reaction:



The Deacon reaction, which is catalysed by metals present in the surface of the flyash, is first order with respect to HCl concentration, and exhibits a rate maximum at 400 °C [128].

Elucidating the influence of chlorine concentration has led to great endeavours, and the form of chlorine present during the formation of PCDD/F has been investigated in a number of ways. In most attempts to study the reaction system, the concentration of Cl in the solid fuel or the concentration of HCl in the gas phase has been the variable controlled and monitored. The concentration of HCl in the gas phase was found to be proportional to the quantity of chlorine added (as PVC) to the feed of both a lab furnace [129] and a 220  $\text{kg h}^{-1}$  incinerator [63]. In the pilot incinerator at Umeå, no distinction was found [130] between the types of chlorine, i.e., organic (PVC) or inorganic ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ) added to synthetic MSW. There was no correlation between the amounts of PCDD/F and PCBz formed and the chlorine content of the feed until the chlorine content approached 1 wt%. A similar result is reported elsewhere for a waste incinerator [131]. On the other hand a clear correlation has been found between the amount of PCDD/F and the chloride content, when various plastics were burned with PVC for 2 h in a pilot-scale combustor [132]. The Cl concentration in the exhaust gases ranged from 2 to 1800  $\text{mg N m}^{-3}$ .

Under conditions where chlorine is freely available, the extra chlorine would mean that any 3-ring phenanthrene structures released are more highly chlorinated, and so more likely fall into the PCDD/F category. Thus in conditions of low Cl, the rate may be controlled by oxygen availability, but under excess Cl it may be proportional to the concentration of free chlorine. This is consistent with an apparent critical chlorine content in the fuel of 1 wt%, as found by Wikström et al. [130]. Below this value, the chlorine content had no influence on the level of PCDD/F emissions, but above this value they rose. With the combustion of the biomass materials wood, straw, hay and triticale, which contain inherently low amounts of chlorine, a general positive correlation between chlorine and PCDD/F yield was apparent [133].

In their factorial experiment using flyash in an entrainment reactor, Gullett et al. [72] examined the influence of added HCl and  $\text{Cl}_2$ . They found that HCl concentration was a significant variable, and increases in HCl always led to more PCCDD. However, above

330 °C an increase in HCl gave lower totals of (PCDD + PCDF). The concentration of added Cl<sub>2</sub> was a less significant variable, but this result may reflect the envelope of experimental conditions chosen. During 24 h tests in an operating MSW incinerator, HCl concentration was controlled by adding dolomite to the feed [86]. A linear relation between the amounts of PCDD and PCDF formed and the concentration of HCl was reported. Although the plot for PCDD against HCl passed through the origin, that for PCDF was steeper and showed an intercept (i.e., a positive amount of PCDF) at zero HCl. This is consistent with the results in the entrainment reactor [72], where much furan was produced in the absence of gaseous chlorine.

The addition of 5 vol% of HCl to the moist air stream in a version of the annealing experiment with 0.5 wt% CuCl<sub>2</sub> led to a threefold decrease in PCDD/F formation [55]. This is explained as the result of two interfering processes: (i) accelerated destruction of PCDD/F, as indicated by a fall in the PCDD to PCDF ratio, and (ii) increased chlorination of the carbon matrix, which stabilises the carbon against burnoff. In the sinter pot tests of Kasai et al. [38], various amounts of chlorine were added in the form of PVC or sodium chloride. It was found that the amounts of PCDD/F formed were approximately proportional to the chlorine added in either form, but with significant scatter at high chlorine loadings (1.05 g g<sup>-1</sup> of mix). Kasai et al. [38] also found that in a pot test the type of carbon somewhat influences the PCDD/F content, but recycled electrostatic precipitator dust produced massive increases.

The influence of the form of chlorine added to a MSW flyash from which PCDD/F had been removed has been examined in a fixed bed reactor [134]. The ash contained 2.0 wt% carbon and 9.1 wt% chlorine; see Table 2. Various fuels such as newspaper, kerosene, polyethylene, and polypropylene were used, with chlorine added either as PVC, NaCl adsorbed onto clay, or as gaseous HCl. The results showed that the flyash is an excellent accelerator of the reactions with added chlorine in all forms, i.e., inorganic, organic, or gaseous HCl. An annealing experiment under 10 vol% O<sub>2</sub> was carried out by Addink et al. [135], in which NaCl was added to MSW flyash from which the organics had been extracted. Even with no added chlorine, significant amounts of PCDD/F were formed from inherent Cl, at a maximum rate of ~1 ng g<sup>-1</sup> s<sup>-1</sup> at 300–310 °C. The system did not respond to the addition of NaCl up to 21% by weight, except when the soluble inorganic chloride in the ash had been removed by washing. The extent of incorporation of external chlorine into PCDD/F was further examined by Addink and Altwicker [136], by means of the <sup>37</sup>Cl isotope present

in Na<sup>37</sup>Cl. The transfer from admixed NaCl is poor, but the addition of CuCl<sub>2</sub> increased the rate by acting as a shuttle. When the CuCl<sub>2</sub> was adsorbed into the matrix by aqueous exchange and evaporation, even higher rates of Cl incorporation into the carbon matrix were found.

The action of HCl and Cl<sub>2</sub> in similar molar concentrations was studied during annealing experiments [83]. Despite the far greater concentration of molecular chlorine present when adding Cl<sub>2</sub>, the amounts of PCDD/F formed were very similar. It was concluded that the Deacon reaction is not a significant player in the chlorination process. However, the fact that the product yields were unchanged suggests that some other process was rate limiting. This may have been carbon, as the activated carbon used as the carbon source was merely mixed with the flyash from which the native carbon had been removed. Thus the catalytic effects may have been minimal.

Recent experiments have indicated that elemental chlorine is the main chlorinating agent [82,137]: ash containing 6.3 wt% chlorine was reacted for 1 s under entrainment conditions in a flow of nitrogen or air [82], to which was added HCl or Cl<sub>2</sub>. Formation of PCDD/F occurred in a downstream section, which cooled the flow from 650 to 240 °C. The addition of Cl<sub>2</sub> greatly increased formation rates, whereas adding HCl alone gave no significant increase over no gas-phase chlorine. HCl in the presence of oxygen led to more PCDD/F, probably due to a predicted rise in Cl<sub>2</sub> concentration. The more reactive ·Cl radical is not present in sufficient concentrations to influence the result. In a sequel to this entrained-flow work [111], the role of chlorine speciation was targeted, namely as Cl<sub>2</sub>, HCl, or free atoms (radicals) of chlorine in the gas phase, and as ash-bound chlorine. The results confirmed that HCl is a poor chlorinating agent, but that Cl<sub>2</sub> increases the PCDD/F yield, especially in the higher chlorinated homologues. A mixture of Cl<sub>2</sub> and Cl atoms did not increase the amount of product under similar conditions. It was concluded that ash-bound Cl was a sufficient source for the observed formation rates of de novo PCDD/F.

By a statistical analysis of the distribution of congeners in PCDF on a flyash, Iino et al. [138] concluded that the presence of less chlorinated congeners was the result of the abstraction of chlorine from higher congeners, i.e., that all congeners tended to begin as OCDF.

#### 3.2.4. Oxygen

Gaseous oxygen is required for the de novo reactions in order to initiate carbon gasification and rearrangement, and to produce elemental chlorine. Addink and Olie [139] investigated the influence of oxygen concentration during annealing tests on acti-



vated carbon and flyash. Zero oxygen does not result in any de novo PCDD/F being produced. As  $O_2$  concentration is varied from zero to 2 mol%, the rate of PCDD/F formation was found to be roughly proportional to the oxygen concentration, but it showed little increase above 2%. Gullett et al. [72] found little influence of oxygen concentration on de novo formation during short residence times with  $[O_2]$  in the range 1.7 to 8.8 mol%. Ryan and Altwicker [125] found a maximum conversion rate at 2% oxygen when using activated carbon in the reaction mixture. This behaviour may be the result of the Deacon reaction, which forms a plateau in HCl conversion at oxygen concentrations above 2 mol% [128].

In contrast, Vogg et al. [110] have reported a continual increase in PCDD/F product from flyash during annealing tests in gases with increasing oxygen content up to 10%. The dependence was linear for PCDD and to the half power for PCDF. The difference may be due to chlorine availability, as the flyash used by Addink and Olie [139] had been heat-treated to remove organics, a procedure which could also have removed volatile chlorine. Alternatively, the limitation at high Cl may be due to inhibition by the large amounts of chlorine; see the section on catalysis. The results of Vogg et al. [110] are indicative of the behaviour of the reaction carbon with  $O_2$ . The order of this reaction with respect to oxygen has been found to be 0.54 for carbon burnoff from a flyash [65], which is similar to the value of 0.5 found for petroleum coke and 0.7 for a coal ash. After testing three flyashes with  $^{18}O_2$  in the gas, Wilhelm et al. [81] found that some were better at incorporating this  $^{18}O$  than others, for which the  $^{16}O$  oxygen came from the ash. Higher chlorinated products contained lower amounts of  $^{16}O$  and vice versa, but there was little isotopic variation within the homologues. The PCDD contained higher amounts of  $^{18}O$  than PCDF. They speculated [81] that the Cu catalyst may transfer gaseous oxygen into the hydrocarbon structures.

This work with isotopes was later extended [140], and after 2 h at 300 °C an average 40% of the PCDD/F products were found to have resulted from the condensation of two 6-ring chlorinated compounds formed by de novo synthesis. The fraction fell with increased reaction time and with increase in temperature. Little PCDF was formed from  $C_6$ -precursors. Various reaction mechanisms, including condensation between a mobile TeCP molecule and one embedded in the carbon matrix, were postulated to explain these results. Olie et al. [104] used tagged oxygen  $^{18}O$  in the reactant gas to establish the source of the oxygen in PCDD/F products during de novo reaction. They found that for furans (one oxygen atom per molecule), the higher homologues contained larger fractions of  $^{18}O$ . The occurrence of

$^{16}O$  indicated that the oxygen was initially present in the solid, either adsorbed or chemically incorporated. With dioxins (2 oxygen atoms), the substitution pattern was not regular. The amount of  $^{16}O$  was higher in the TeCDD fraction, and mixed  $^{18}O^{16}O$  products were never more than 35 mass% of the total. Olie et al. [104] concluded that the higher chlorinated compounds incorporate gaseous oxygen, while the lower ones use bonded oxygen to form PCDD/F. Dioxin-like structures must have been present in the carbon matrix and were released during oxidation, especially in the case of the lower chlorinated homologues. Wilhelm et al. [81] repeated these experiments and came to similar conclusions.

The form of chlorine released during the pyrolysis of PVC has been investigated by Kanters et al. [129]. Various amounts of PVC up to 5 wt% were added to a simulated MSW containing 0.46% of Cl, and incinerated batchwise under air at 850 °C. The quantity of chlorophenols released into the gas remained virtually constant at 3.3  $\mu\text{mol/kg}$  of dry waste at all levels of PVC addition. The chlorine was lost as HCl at 82% recovery. This result implies that PVC will not contribute precursors to PCDD/F formation, but will make HCl available for de novo reaction. The presence of water vapour was found to enhance PCDD/F formation, especially of the lower homologues, Pe and Hx [110]. This was shown to be partly the result of dechlorination of the higher homologues.

### 3.2.5. Particle size

One variable which has attracted little attention and needs further investigation is particle size. Differences in PCDD/F concentrations on a mass basis among particles of different size have been regularly noted (e.g., [14,141]), but little appreciated. For example, when a cyclone was added to the outlet of the combustor section at Umeå, the ash taken from the cyclone was compared with that leaving the convection section [131]. There was a slight difference in congener distribution between them, but the total amount of PCDD/F in the exit was almost the same, because it was concentrated in the fines which had escaped from the cyclone.

When the surface reactions on flyash were examined, attention has tended to focus on the carbon, despite the fact that no correlation has been found between PCDD/F yield and carbon surface area [122]. For reasons outlined below, the global (external) surface area appears to be a better basis for quantifying reaction rates. Following an analysis of incinerator flyash, Fängmark et al. [142] concluded that chlorinated organics tend to be concentrated on the smaller particles. A similar result has been reported by Ruokojärvi et al. [143], where the < 1.6- $\mu\text{m}$  fraction was disproportionately loaded. The distribution

of PCDD/F with particle size in atmospheric dust collected at four Japanese sites was examined by Kurokawa et al. [144]. The maximum size collected was  $\sim 30 \mu\text{m}$  in aerodynamic diameter, and the smallest  $0.1 \mu\text{m}$ . Particles less than  $1.1 \mu\text{m}$  contributed 50% of the total PCDD/F, with an almost equivalent I-TEQ proportion. The distribution of homologues changed with size, with the fraction of less chlorinated congeners in the homologue groups increasing with increasing particle size.

The use of external surface for reaction analysis is consistent with the results for MSW ash of Mätzing et al. [77]; they found that the global area was similar to the BET area, suggesting that the particles had negligible porosity. Hinton and Lane [145] after extensively characterising the ashes from 13 MSW incinerators concluded that “comparing the electron micrographs, mercury porosimetry and surface area data suggests that the majority of the surface area is found on the exposed surfaces of the flyash rather than the internal pores.” In addition, Collina et al. [78] deduced from the equilibrium loadings during their OCDD adsorption tests onto flyash that only a few percent of the BET area was present as active sites. The area reported by them was in fact similar to the global area of the particles ( $d_p < 200 \mu\text{m}$ ). The results of Ryan and Altwicker [125] on two carbon blacks showed that the external surface area of the spherules was the significant variable.

Two samples of MSW ash which were screened into three particle sizes, namely  $+800$ ,  $-350 + 150$ , and  $-38 + 20 \mu\text{m}$ , were found to have uniform surface concentrations of PCBz, PCP, PCDD, and PCDF for the three sizes [70]. This uniformity was found despite the fact that the amount of carbon present, which could act as an adsorbent, varied greatly (Table 2). The annealing at  $300^\circ\text{C}$  of these three size fractions of MSW flyash above was traced on the basis of PCDF content, normalised for the external (global) surface area and the carbon and chlorine contents by the empirical variable

$$\phi = \frac{3[\text{PCDF}]}{d_p[\text{C}][\text{Cl}]} \text{ mol}_{\text{PCDF}} \text{ m}^{-2} [\text{C}]^{-1} [\text{Cl}]^{-1},$$

where  $d_p$  is the particle diameter ( $\mu\text{m}$ ) and  $[\text{PCDF}]$ ,  $[\text{C}]$ , and  $[\text{Cl}]$  are the concentrations of PCDF, carbon, and chlorine, respectively. Figure 5 depicts the change of  $\phi$  with time for PCDF content, with the carbon content updated for burnout. The plots are linear and roughly equivalent for the three particle sizes: this suggests that the carbon and chlorine act simply as reactants. The lines are straight because at  $300^\circ\text{C}$  the destruction reactions are less significant than those of formation. A similar plot was found for PCDD [70]. A different situation may apply at  $350^\circ\text{C}$ , as the equivalent test at this temperature [70]

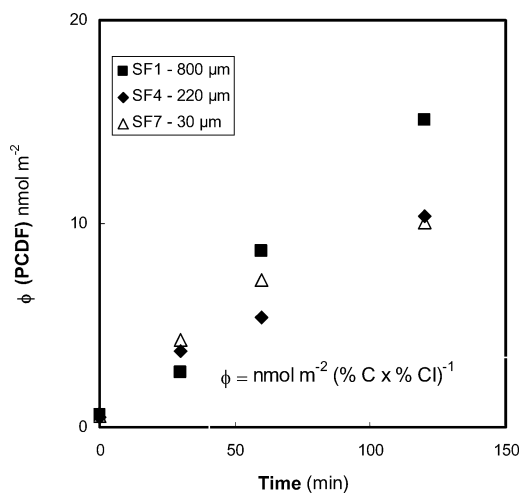


Fig. 5. Development of the value of  $\phi$  (the normalised PCDF content) during annealing of 3 MSW flyash sizes [70].

produced PCDF concentrations, which were not related to surface area. When  $\phi$  for the concentration of PCDF product was normalised only for the carbon and Cl contents (and not area), it was constant at approximately the same value for the three sizes. This implies that the two reactants are active throughout the whole particle, which may reflect a higher mobility for copper within the ash matrix at the higher temperature. The constant value of  $\phi$  indicates that a dynamic equilibrium between the formation and the destruction reactions was quickly achieved.

### 3.3. Destruction reactions on the solid phase

The effects of dechlorination and destruction of PCDD/F on the surface of a particle must be considered. Vogt and Stieglitz [146] collected incinerator flyash from an ESP and analysed it for PCDD/F. They then simply heated it in air for 2 h at temperatures between  $120$  and  $600^\circ\text{C}$  and found that extra PCDD and PCDF could be formed under certain conditions. At  $200^\circ\text{C}$  the concentrations were slightly less than the nontreated ash, but at  $300^\circ\text{C}$  increases in concentration by factors of 10 to 15 were observed. At  $400^\circ\text{C}$  the values were far less than the original, while at temperatures of  $500$  and  $600^\circ\text{C}$  all the PCDD/F were effectively destroyed. Similar work was done on material adsorbed onto an alumina substrate [147], but no kinetics were established in either program.

Following some experimental measurements of the decrease in PCDD/F on flyash following thermal treatment, an empirical relation in the form of an exponential decay was developed by Lasagni et al. [148]. Exponential parameters were developed for the different congeners. Subsequently the destruction of the parent compounds biphenyl, DD, and DF

on an activated carbon/silica substrate was studied under different atmospheres [149]. Another experiment of this kind involved the destruction of OCDD and OCDF on copper powder [150], but this condition is unrealistic for incineration studies. Collina et al. [78] measured the rates of thermal destruction of OCDF and OCDD when adsorbed onto a flyash. The furan homologues are more stable than the equivalent dioxins. Both dechlorination and destruction reactions were identified. Destruction became more prominent at higher temperatures and was virtually the only reaction at 300 °C. The presence of water vapour accelerated the reaction by almost an order of magnitude. The decomposition and dechlorination reactions of 123478HxCDD adsorbed onto flyash were examined at 218 and 248 °C by Addink et al. [151]. These low temperatures were chosen to avoid devolatilisation of the adsorbed material. When HCl was present in the gas phase, chlorination rather than dechlorination/decomposition was the dominant reaction. A study of the dechlorination of both native and adsorbed PCDD/F on flyash under pure nitrogen at 340 °C was undertaken by Stach et al. [152]. About 98% removal was achieved after 6 h. The extent of decomposition was similar for the dioxins and furans, except for the Te and Pe congeners, where greater stability was exhibited by the dioxins.

The emission of PCDD/F is controlled in industrial processes either by adsorption, e.g., with activated carbon, or by thermal destruction over a catalyst. For example, a commercial catalyst pack of platinum on Ti/SiO placed in the flue-gas duct of a MSW incinerator was found to be effective in destroying most of the PCDD/F [153]. PCDD/F catalysts tend to be effective also for NO<sub>x</sub> removal [154]. The emission of PCDD/F from operating incinerators is controlled by carbon addition [155,156]. The reaction between the PCDD/F and the OH radical at ambient temperature (297 K) was studied by Kwok et al. [157], and kinetics for this temperature were established for atmospheric modeling.

### 3.4. Catalysis

The inherent carbon in flyash is much more reactive than carbon mixed with synthetic mixtures based on silica, probably due to the intimate contact between the metallic catalysts distributed within the ash and the carbon. The effect of the proximity of a catalyst is illustrated by the work of Neeft et al. [158] on the oxidation of carbon black. They found that some metal-based catalysts were far more efficient when ground with the carbon for extended periods, than after simple mixing of the powders. A range of metals has been examined in annealing tests to establish relative activities (e.g., [94,97,159,160]). Stieglitz

et al. [97] varied carbon type and concentration, and a number of metals in experiments containing flyash or Mg–Al–SiO<sub>3</sub>/carbon/KCl/MCl at 300 °C. Only copper was found to be active; in fact Mg, Zn, Fe (II), Mn, Hg (II), Cd, Ni, Sn (II), and Pb (II) produced no measurable PCDD/F. The authors varied the concentration of copper from zero to 0.4 wt% and found a continual increase [97], although the homologue distribution changed to favour the Hx and H groups at the higher copper levels. In contrast, the addition of 0.07% of copper as CuCl<sub>2</sub>·2H<sub>2</sub>O to a synthetic waste of paper pulp, flour, and sawdust led to only a 30% increase in PCDD/F formation [160]. Its main effect was to increase the extent of chlorination. Gullett et al. [94] found that copper is ~10 times more active than nickel, which is in turn 10 times more active than iron.

Olie et al. [104] found that during annealing tests, operation with an iron catalyst required higher temperatures than copper to give equivalent production rates of PCDD/F. In contrast, Halonen et al. [160] found that iron was nearly as effective as copper in a 32-kW pilot combustor. For each metal, the conversion to PCDD/F under different combustion conditions (poor/good) responded differently for gas and particles. Under poor conditions, particle concentrations rose while gas-phase concentrations fell.

In their annealing experiments at 275 °C with activated carbon, Ryan and Altwicker [125] have reported a linear increase in the yield of PCDD/F, when the concentration of ferrous chloride was increased from 1 to 21 wt%. The role of copper was investigated by Luijk et al. [55] in flowing moist air with 5 mol% HCl over activated carbon at 300 °C. Increasing the concentration of CuCl<sub>2</sub> from 0.1 to 0.5 wt% resulted in a sharp drop in the yield of PCDD/F. The original yield was only restored by adding 5 wt% CuCl<sub>2</sub>. As before, an increase in catalyst loading tended to produce more highly chlorinated congeners. Copper as CuCl<sub>2</sub> was active [55] in the chlorination and condensation of acetylene to HxCBz under HCl at temperatures of 200 to 400 °C. An explanation for the rapid fall in oxidation rate during de novo formation may be the availability of catalyst. The carbon adjacent to a catalyst particle is consumed, so that contact worsens with burnout. The low Tammann temperature [161] for copper salts suggests a high mobility for the metal at low temperatures, but due to the dispersed nature of the carbon, it may not all be easily accessible. Intimate dispersion of the catalyst in carbon is essential for high activity during the oxidation of carbon [158].

When ashes from MSW were sampled from the precipitator hoppers of 13 small incinerators, the concentration of PCDD/F was found to correlate with the copper contents [145]. No correlation was found with the carbon content, mean particle size, or the BET sur-

face area of the ashes. This is not surprising in view of the diverse operating conditions in the incinerators and variations in the properties of these wastes. There was, however, a correlation between the copper and the PCDD/F contents normalised for surface area ( $\text{ng m}^{-2}$ ).

There are many reports of a fall in the rate of the reactions producing PCDD/F in the presence of inhibitors such as sulfur and nitrogen compounds, during laboratory tests. Addink et al. [162] tested the nitrogen compounds EDTA (ethylenediamine tetraacetic acid) and NTA (nitritotriacetic acid), as well as sodium sulfide in a laboratory furnace. Reductions in PCDD/F of the order of 90% were readily attained, and the ratio of PCDD/PCDF fell. Thermodynamic control was indicated, as the same distribution of isomers in the homologues was retained. Similar tests with various organic amines added at 2 wt% concentration produced > 99% removal [163]. The addition of 400 ppm of ammonia to a synthetic flue gas during an annealing test was found to reduce the amount of PCDD/F present by 85% [110]. Mixtures of amines have been used successfully at 400 °C in a pilot plant [165], and the amides of sulfuric acid are also effective. The amines appear to deactivate the copper surface by forming nitrides. Inhibition is also found in larger scale tests, such as with the 10 kg h<sup>-1</sup> pilot MSW incinerator [4], where sulfur-containing fuel oil was used for a secondary flame. In a pilot-scale combustor burning natural gas to which flyash and HCl had been added, inhibition by sulfur occurred at S/Cl ratios as low as 0.64 [165]. The tests showed that the action of molecular chlorine is inhibited by SO<sub>2</sub> in the gas phase, in addition to any effects S may have on the copper catalyst.

Ruokojärvi et al. [166] found that the addition of sulfur and nitrogen compounds to a pilot-scale plant reduced the emissions of PCDD/F and chlorophenols, but had little effect on the ratio of PCDD to PCDF. The additives were particularly effective on the particulates. They proposed that inhibition occurs before precursors form on the surface. On a still larger scale, the co-firing of bituminous coal containing sulfur in a commercial incinerator burning MSW produced a significant decrease in PCDD/F emissions, with memory effects due to adsorption on the wall [167]. A similar result was found when lignite containing 1.6 wt% sulfur was added to MSW [168].

Tupperainen et al. [30] have postulated some possible mechanisms for the inhibition of PCDD/F formation by sulfur. With nitrogen compounds, PCDD/F production is hindered on a particle's surface during the early steps of the formation chain [169]. Gullett et al. [126] have suggested that SO<sub>2</sub> may deplete Cl<sub>2</sub> levels by converting it to HCl. Alternatively, CuCl<sub>2</sub> may be preferentially converted to the sulfate, which

is inactive. Mätzing et al. [77] found that urea was an effective inhibitor when added to a pilot-scale furnace. Ruokojärvi et al. [143] performed similar tests in a pilot furnace burning synthetic MSW, and found a diminution in PCDD/F by three quarters when 1 wt% urea was added. The same reduction was found across all particle sizes, indicating a surface reaction. The more highly chlorinated congeners suffered the greatest reduction. When added as Ca(OH)<sub>2</sub>, calcium inhibited the formation of PCDD/F during annealing tests [46], but not when added as CaCO<sub>3</sub>. The explanation given is that the effect was due to an increase in basicity, and not specifically to the calcium. Control of PCDD/F formation by adding calcium hydroxide also occurred in the entrainment tests of Gullett et al. [72].

### 3.5. Comments

The consensus of evidence on de novo formation supports the view that the rate of formation of PCDD/F is proportional to the amount of carbon present and to the rate of its oxidation. The surface area of the carbon is not a significant variable. The concentration of oxygen in the gas is important only up to a value of 2 mol%, above which it has little effect. Copper plays a central role not only as a catalyst for the basic reactions, such as the oxidation of carbon, the chlorination of the carbon matrix, and its dechlorination, but it also acts as a source of chlorine. In most ashes such as from MSW, the inherent concentration of copper is not a rate-limiting feature, in contrast to extraneous copper mechanically mixed into a synthetic ash. For MSW ash at 300 °C the reactions occur on the surface of the particles, but activity in the interior may occur at higher temperatures.

There are two aspects of the heterogeneous formation of PCDD/F requiring resolution. The first is the relative importance of the precursor versus the de novo route, and the second is the role of chlorine in the de novo system. With regard to the former, the claim of Huang and Buekens [34] that de novo is the dominant route in MSW incinerators was based on two aspects: (i) the congener fingerprint of the products and (ii) the result of modeling of the conditions in an incinerator. Their model uses kinetics derived from laboratory experiments by Milligan and Altwicker with chlorophenols on MSW ash. Even with a worst case scenario with a PCP concentration of 1000  $\mu\text{g N m}^{-3}$ , the predicted PCDD level is 10<sup>-3</sup>  $\mu\text{g N m}^{-3}$ , i.e., minimal. After a review of thermal processes involving the incineration of MSW, wood and other waste, boilers, and metals processing, Everaert and Baeyens [170] come to the same conclusion. This conclusion was reinforced by the experimental data of Hell et al. [98], and the model of Stan-

more [171]. On the other hand, recent experiments by Mulholland and Ryu [99] in a packed bed found extremely high rates of PCP conversion. In those experiments, the conversion on a 1 g bed of 325-mesh particles was mass-transfer limited. It follows that the actual chemical kinetics were even faster, and hence unknown. If the mass-transfer coefficient derived from those experiments, namely  $6 \times 10^{-5} \text{ m s}^{-1}$ , is assumed to be the kinetic rate for 30- $\mu\text{m}$  ash particles in the gas stream of a typical incinerator, the formation rate of PCDD/F is of the order of  $0.1 \text{ ng g}^{-1} \text{ s}^{-1}$ , i.e., negligible. The chemical kinetics would need to be orders of magnitude faster for this route to become significant.

Unraveling the role of chlorine in de novo chemistry is difficult, because chlorine is present in a number of forms, such as HCl, Cl<sub>2</sub>, and Cl<sup>·</sup> in the gas phase, or as inorganic or organic Cl in the solid, or associated with the copper catalyst. It appears that there is sufficient chlorine in most ashes, viz. 5 wt%, to adequately account for de novo formation. When gas-phase chlorine is active (as Cl<sub>2</sub>), it supplies Cl to replace the depletion experienced by CuCl<sub>2</sub> after it has chlorinated the solid by disproportionation.

#### 4. The kinetics of the formation and destruction of PCDD/F

Altwickler [172] has noted that the net formation rates on the ash passing through the gas ducts of incinerators are of the order of 150 to 15,000 ngPCDD/F g<sup>-1</sup> s<sup>-1</sup>. If the ash concentration is a typical 0.5 g N m<sup>-3</sup>, this is equivalent to 75 to 7500 ngPCDD/F N m<sup>-3</sup> s<sup>-1</sup>. In the furnace section (gas phase) of MSW incinerators, Shin et al. [5] have reported values of the order of 6 ngPCDD/F N m<sup>-3</sup> s<sup>-1</sup>. Thus the rates in the low-temperature section (homogeneous reactions) are much higher than in the furnace section (heterogeneous reaction). The emissions from an iron sinter strand were quoted by Buekens et al. [14] as 3–15 ngI-TEQ N m<sup>-3</sup>, similar to levels during the incineration of MSW. Unsteady state conditions in combustion systems such as incinerators and steel furnaces lead to enhanced emissions [15,173]. There is a memory effect after transients in an MSW incinerator, in that the high levels of PCDD/F persist for many hours after the event. It has been postulated that carbonaceous deposits on the duct walls first trap and then release these components.

##### 4.1. High-temperature (homogeneous) reactions

After the discovery of solid-phase reactions in incinerators, it was realised that they contributed most

to the I-TEQ in the stack. Accordingly, interest in control techniques has focused on the solids. Now that high-quality systems for particulate removal are universal in new industrial plants, the proportion of gas-phase I-TEQ in emissions has risen, although the total levels have fallen. Hence more attention is now being given to gas-phase reactions.

At the exit of a combustor where temperatures are 700 °C or higher, it can be assumed that all the PCDD/F are present in the gas phase. This follows both because at this temperature they would favour the vapour phase and because they are rapidly destroyed above 400 °C on the ash's surface. It was found in a small two-stage combustor burning simulated MSW, where the primary and secondary chambers were run independently at temperatures of 700, 800, and 900 °C, that a strong maximum in PCDD/F formation appeared when the primary chamber was at 700 °C and the secondary at 900 °C [33]. The measured exit concentrations of PCDD/F from the high-temperature furnace (boiler) sections of five commercial MSW incinerators reported by Shin et al. [5] ranged from 0.8 to 5.7 ngI-TEQ N m<sup>-3</sup>. The values reported at the furnace outlet by Sakai et al. [7] were 80 ngPCDD/F N m<sup>-3</sup>, i.e., in the same range. Düwel et al. [13] found ~400  $\mu\text{g}$  of PCDD and 1000  $\mu\text{g}$  PCDF per ton of C as CO<sub>2</sub> while incinerating MSW. For a typical incinerator flue gas of 10 mol% CO<sub>2</sub>, these values are equivalent to 20 and 50 ngPCDD/F N m<sup>-3</sup> of flue gas, respectively. Most reported values are therefore in the range 10 to 80 ngPCDD/F N m<sup>-3</sup>. Such a restricted range may reflect the comparative insensitivity of the reaction to temperatures above 700 °C, as indicated by the experimental measurements in Fig. 3.

A rough estimate of the rate of formation of PCDD/F in the gas phase can be deduced from the results of Sidhu et al. [51] shown in Fig. 3. Assuming a simple first-order reaction, the formation rate constant calculated from their experiments at 700–800 °C is  $0.1 \times 10^{-3} \text{ s}^{-1}$ . With a concentration of chlorophenol in the feed of 20  $\mu\text{g N m}^{-3}$ , which is typical of that in an MSW incinerator [35], this would produce 2 ngPCDD/F N m<sup>-3</sup> s<sup>-1</sup>. The latter figure agrees with the measured formation rates. Shin et al. [5] have suggested a 5-s residence time for furnaces; this gives net formation rates of 0.15 to 1.2 ngI-TEQ N m<sup>-3</sup> s<sup>-1</sup> for their data, with a mean of 0.5 ngI-TEQ N m<sup>-3</sup> s<sup>-1</sup>. Taking their value of 12 for the ratio of PCDD/F to I-TEQ, this gives a PCDD/F equivalent of 6 ngPCDD/F N m<sup>-3</sup> s<sup>-1</sup>, which is of the same order as estimated from Sidhu et al.'s results [51]. The net formation rates in the high-temperature section of the pilot-scale fluidised bed at Umeå burning MSW [58] were ~10 ngPCDD N m<sup>-3</sup> s<sup>-1</sup> of PCDD and 25 ngPCDF N m<sup>-3</sup> s<sup>-1</sup> of

PCDF, i.e., in the same range as commercial incinerators.

For the homogeneous situation, Shaub and Tsang [174] have given an extremely high activation energy of  $335 \text{ kJ mol}^{-1}$  for the decomposition reaction. Sidhu et al. [51] found these values adequate for simulating their experimental results, as shown in Fig. 3. Much more work remains to be done in the field of heterogeneous kinetics, as will be discussed in Section 5 on modeling.

#### 4.2. Low-temperature (heterogeneous) reactions

Important work on the adsorption and reaction of a precursor has been carried out by Milligan [175] in an isothermal fixed bed. Studies on the adsorption of 2346TeCP onto flyash have indicated a range of activities for the sites. Thus, Altwicker [172] has postulated the existence of “superactive” sites to explain the high reactivities found in the short term. Hell et al. [66] have measured the rate of formation of PCDD from PCP adsorbed onto flyashes in batch experiments; they found a first-order reaction, with rate constants at  $300^\circ\text{C}$  of the order of  $10^{-4} \text{ s}^{-1}$ . Under similar conditions in a bed of silica doped with  $\text{CuCl}_2$ , Mulholland and Ryu [99] found a much higher rate constant for mixed DCPs. Since this was a continuous reactor using gas-phase PCP, it is more realistic situation.

With precursors a first-order dependence on concentration has been reported by Cains et al. [69] and Milligan and Altwicker [176]. However at low concentrations of precursor, this has been questioned by Huang and Buekens [89] and Penner et al. [177], who have all postulated a second-order dependence. In contrast to the *de novo* reaction, oxygen has been found to diminish the yield from precursors, probably by adsorbing onto active sites [175]. After examining the literature, Gullett et al. [72] concluded that there is sufficient time in the downstream section of a MSW incinerator for the formation *de novo* PCDD/F to occur; their entrainment experiments bear this out. The formation rate in their equipment under typical furnace conditions was  $1200 \text{ ngPCDD/F g}^{-1} \text{ s}^{-1}$ , which is midrange in the values proposed by Altwicker [172] for operating incinerators. Values of this order have also been reported from waste in the pilot incinerator at Umeå [58]. On the other hand the rates of *de novo* PCDD/F formation measured in annealing tests were two orders of magnitude less, but were usually measured after extended reaction times ( $> 30 \text{ min}$ ). They fall with time of reaction; for example, a synthetic flyash held for 1 min at  $300^\circ\text{C}$  formed PCDD/F at a mean rate of  $15 \text{ ng g}^{-1} \text{ s}^{-1}$  [114]. This figure had fallen to less than  $2 \text{ ng g}^{-1} \text{ s}^{-1}$  after 30 min. It is possible that the rate in the first few seconds is much like the rapid rates measured *in situ*.

The carbons present in three flyash samples taken from MSW precipitators were burned by Milligan and Altwicker [65] in a stream of 10 mol% oxygen. The oxidation rate fell only slightly over a time of 30 min, and after 1 min of burning at  $300^\circ\text{C}$  was  $0.00012 \text{ g g}^{-1} \text{ s}^{-1}$ . The activation energies for the oxidation of carbon in the ashes from three separate MSW incinerators were 142, 105, and  $125 \text{ kJ mol}^{-1}$ , respectively, whereas uncatalysed carbon normally exhibits an activation energy of  $\sim 170 \text{ kJ mol}^{-1}$  [178]. The fall in value can be ascribed to catalytic activity. At a temperature of  $300^\circ\text{C}$ , there was an order of magnitude difference between the oxidation rate of one ash and the other two. The mean order of reaction of oxygen with carbon was 0.54. Milligan and Altwicker [65] found that the activation energy fell with time when burning activated carbon and carbon black in similar tests, but this did not occur with any of the carbon from MSW ash. The ashes were far more reactive than a coal ash tested at the same time, and the ratio of  $\text{CO}_2$  to  $\text{CO}$  in the product gas was of the order of 10 rather than 2. A similar increase in  $\text{CO}_2/\text{CO}$  ratio has been found during the catalysed combustion of soot [179].

Stieglitz and co-workers [68,118] investigated the reactivity of carbon in flyash during annealing experiments. They found that  $\text{CO}_2$  was the main product, released at a decreasing rate during carbon removal at constant temperature. For the initial flyash, there was one endothermic peak at  $\sim 350^\circ\text{C}$  with an enthalpy of reaction of  $22.9 \text{ kJ kg}^{-1}$ . A second endothermic peak appeared at a higher temperature after the samples had been annealed for more than 30 min. Stieglitz and co-workers [68,118] found that carbon reactivity fell while annealing reactions proceeded, and their measurements for some 2-h tests pointed to the presence of two rate periods [68]. Two exponential rate expressions were fitted to the carbon burnout data, the first giving an initial rapid rate, and the second a slow burnoff. The oxidation rate calculated after 1 min of reaction at  $300^\circ\text{C}$  is dominated by the initial term and equals  $0.00014 \text{ g g}^{-1} \text{ s}^{-1}$ , which is very similar to the almost-constant rate reported by Milligan and Altwicker [65]. The fraction of gasified carbon being converted to PCDD and PCDD fell with increasing temperature and was  $\sim 5 \times 10^{-6}$  for both species at  $300^\circ\text{C}$ . This is equivalent to a formation rate of PCDD/F of  $\sim 1 \text{ ng g}^{-1} \text{ s}^{-1}$ , which is far smaller than *de novo* rates in incinerators. The annealed carbon on which these rates were measured may not be representative of the condition of newly formed carbon in the ash leaving the high-temperature regions of a boiler. On cooling and storage, the adsorption of atmospheric oxygen may form stable complexes, which inhibit further oxidation [179]. When one extrapolates the annealing data (e.g., [68]) to very short periods

(seconds), the results indicate much higher reaction rates than customarily reported.

The kinetics of formation of PCDD/F on a flyash substrate at 300 °C have been studied by Lasagni et al. [148]. An exponential growth model was fitted, and coefficients for the various congeners were determined. This empirical approach has application limited to the specific conditions of the test. The kinetics of destruction were similarly measured. Conesa et al. [180] used differential thermal gravimetry to study the oxidation of an activated carbon mixed with either CuO or CuCl<sub>2</sub> under an atmosphere containing HCl. The activation energy for the oxidation of pure carbon was 158 kJ mol<sup>-1</sup>, typical of this material, but fell to 121 kJ mol<sup>-1</sup> in the presence of CuCl<sub>2</sub>. An intermediate value was found for CuO in the presence of HCl. A maximum for the rate of formation of PCDD/F appeared at temperatures just below 400 °C. Lower values for the activation energy and the temperature at which the rate is a maximum can be anticipated when the copper is intimately mixed with the carbon, as in flyash.

Despite numerous qualitative examinations of the behaviour of PCDD/F under destruction conditions, only a few kinetic studies have been performed. The destruction of 123478HxCDD adsorbed onto flyash was studied by Addink et al. [151]. An exponential decay was apparent with half-lives of ~25 min at the two temperatures tested. In similar tests Lasagni et al. [148] also found an exponential decay of the congener groups, with 80 to 90% of the material destroyed in 100 min at 300 °C. Collina et al. [78] divided the energetics of the reaction into the adsorption and reaction components. When allowance was made for the energy of adsorption, the true activation energy for the destruction of OCDD adsorbed onto flyash was estimated to be 127 kJ mol<sup>-1</sup>, with a frequency factor of  $3.6 \times 10^{12} \text{ s}^{-1}$ . Previously, values of 157 kJ mol<sup>-1</sup> and  $1.7 \times 10^{11} \text{ s}^{-1}$  had been reported [181].

The rate constant for the decomposition of OCDD at 300 °C was  $1.5 \times 10^{-3} \text{ s}^{-1}$  in the presence of water vapour [78], which should be compared with a formation rate constant from PCP [77] of  $1 \times 10^{-4} \text{ s}^{-1}$ . The latter rate relates to the concentration of PCP in the gas phase, which is generally orders of magnitude higher than the surface concentration of PCDD/F. Thus at 300 °C the formation reaction dominates over destruction. In view of the apparent difference in bonding in Section 2.2 between ash and product PCDD/F formed via the two heterogeneous mechanisms, i.e., from adsorbed PCPs and that formed de novo, it must remain uncertain whether they also exhibit differences in the kinetics of destruction.

#### 4.3. Comments

There is a paucity of experimental information on reaction rates in the gas phase, and only one feed material, i.e., 246TCP has been adequately trialled [51]. More effort needs to be expended in examining a range of heterogeneous reactions. From the PCDD/F concentrations measured on ash sampled directly from flue gas, it can be inferred that newly formed ash is much more reactive than ash which has been recovered, stored, and used for annealing tests. There is no doubt that the reactivity of ash toward the precursor and de novo reactions decreases markedly with time at elevated temperatures. In the de novo case it has been shown that the carbon loses reactivity [68], but this does not explain the large difference in rates. Entrainment experiments offer the best technique for confirmation of high intrinsic formation rates.

### 5. Modeling the generation of PCDD/F in thermal systems

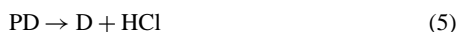
The models developed so far have dealt only with the total entity “dioxins”; I-TEQ values have not been considered. However the environmental application of dioxin emissions deals with I-TEQ values, so that a ratio of PCDD/F to I-TEQ must be invoked in order to relate the two. Before examining detailed chemical models of formation, two general approaches can be noted. A global statistical approach to emissions from incinerators of MSW has been presented by Chang and Chen [182], who used genetic programming and neural network modeling to process output data from incinerators. The genetic program step was incorporated to identify the most likely formation pathways for training the neural network. The authors offered the approach as an efficient way of estimating emissions from conventional incineration.

The technique of CFD has been applied to dioxin modeling by Peche [183] as part of the MiniDIP project, using Fluent to simulate gas flows and particle trajectories in a sinter bed. The input formation rates were supplied on a mass basis as a function of temperature, derived from experimental measurements. The output indicated different concentrations of PCDD/F for different particle sizes, due to their different residence times in the various temperature zones. CFD modeling of the combustion regime in MSW furnaces has been undertaken by Hunsinger et al. [184] and by Gan et al. [185], but only the latter included the dioxin-forming reactions. The ultimate application of the models discussed below should be as input data for such CFD approaches.

One of the major difficulties in producing workable models is the lack of experimental data produced under controlled conditions, with which the models can be validated. In the gas phase only one reliable set of measurements is available [51], and this concerns only one reactant, namely 246TCP. The ideal (and presently unrealisable) model would incorporate every reactant and all processes. With respect to heterogeneous reactions, most of the laboratory tests carried out with solids, e.g., on incinerator flyash and sinter plant ash, have been carried out over comparatively long periods. They therefore do not simulate the conditions under which the ashes were formed, and the applicability of the results to incinerator modeling must be doubtful. Typical rates measured in incinerator furnaces are 10–1000 ngPCDD/F g<sup>-1</sup> s<sup>-1</sup>, while in laboratory tests it is 0.1–1 ngPCDD/F g<sup>-1</sup> s<sup>-1</sup>.

### 5.1. Homogeneous reactions

The first significant attempt at modeling the formation of PCDD, by Shaub and Tsang [174] was addressed primarily to the gas phase. The model considers chlorophenol precursors and takes account of the combustion environment through temperature and the concentrations of reactants. The intermediate organic species reacting to give PCDD (designated as D) were considered to be polychlorinated phenols (P), polychlorinated phenoxy radicals (P\*), polychlorinated 2-phenoxyphenols (PD), and organic fuel compounds R. Any unspecified product is designated as Pr. The reactions in which these species participate were given as



This scheme assumes that the phenolic (single ring) precursors form radicals, which can condense to phenoxy (double ring with an oxygen linkage), and

then to PCDD. The OH radical is taken to be the most active oxidising species under combustion conditions. All the species may pyrolyse or oxidise to waste products in reactions (3), (13) and (8)–(11). The rate constants for reactions (1) to (13) were estimated from the literature for similar reactions. The rates for reactions (2), (6), (8) and (10)–(12) are independent of temperature. The equations for the above mechanism were solved for various temperatures and reactant concentrations (chlorinated phenols and fuel-derived organic molecules). The predicted concentrations of DD were in order-of-magnitude agreement with contemporary measurements under incinerator conditions. It has subsequently been shown by Khatchatryan et al. [186,187] that the rates predicted by this gas-phase model were underpredicted for two reasons. First, the possibility of radical-radical recombination was underestimated, and secondly, the resonance stabilisation of the phenoxy radical was not recognised. As a result of the latter, the rate of destruction of the 246TCP radical by oxygen was grossly overestimated by Shaub and Tsang.

Sidhu et al. [51] employed the model of Shaub and Tsang [174], but decreased the activation energy for the condensation reaction (4) to fit their own experimental work. The result is depicted in Fig. 3, where the agreement is only fair. However, the complexity of the reactions makes this type of modeling very difficult. Babushok and Tsang [188] have considered a combustion sequence of localised mixing and reaction, where free chlorine is produced in fuel-lean systems, leading to the production of chlorinated phenoxy radicals when mixed into a fuel-rich region. The phenoxy radicals can then go on to produce dioxins. The kinetic scheme which they put forward for incinerator conditions predicts yields of PCDD/F of the correct order of magnitude.

The Shaub and Tsang approach [174] was modified by Khatchatryan et al. [186,187] by taking account of new kinetic information on the stability of phenoxy radicals to produce an expanded (45 reaction) and a core (12 reaction) model. The reaction scheme, which involves over 30 chlorinated species including stable molecules, radicals, and intermediates, proposes the OH radical as the most reactive centre. The expanded model when solved with CHEMKIN gives a good simulation (see Fig. 3) of the experimental results of Sidhu et al. [51] for the conversion of 246TCP to 1368TeCDD. The core model does not perform quite as well.

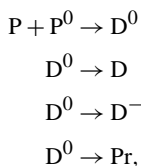
Other more simple models have been developed to incorporate into general models of a furnace. To estimate the amounts of pollutant leaving an incinerator, Chagger et al. [189] have proposed a gas-phase system involving precursors, which react under the influence of ash-borne catalyst. The concentration of



PCDD/F product was calculated as a function of precursor concentration, temperature, and oxygen concentration. An unlikely outcome is that an increase in the concentration of O<sub>2</sub> from 6 to 24 mol% produces a 10-fold increase in the production of PCDD/F. Stanmore [171] has taken a formation to occur in a single step with an activation energy based on the condensation step, coupled with thermal decomposition via one first-order reaction. The approach is unable to simulate Sidhu's data adequately, but does reproduce the maximum at 900 °C found in a two-stage combustor [33]. Also it gives reasonable agreement with measurements in the Umeå pilot-scale fluidised bed [56]. The latter data represent a collection of PCDD/F compounds and not one pathway only.

### 5.2. Heterogeneous reactions

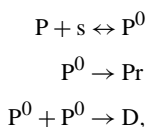
As noted earlier, the data used for validating heterogeneous models have often been derived from annealing tests lasting more than 30 min. However, the passage of ash through the gas ducts of a combustor often takes only seconds. Another criticism which can be leveled against most existing models of heterogeneous formation is in the failure to take proper account of the nature of the ash's surface, particularly with respect to particle size. Surface models are necessarily empirical in nature, because the mechanisms of adsorption and reaction are complex, and have not been adequately elucidated. In a first attempt at modeling production involving the solid phase, Shaub and Tsang extended their model [190] by considering the reactions to take place in the gas, and the product to subsequently adsorb onto the solid. This was clearly inadequate, but the approach was developed by Altwicker et al. [191] to consider surface coverage in a four-step model comprising reaction, desorption, dechlorination, and decomposition. The dechlorination of species was accommodated by including the species D<sup>-</sup>, which is at a lower chlorination level than originally formed PCDD/F.



where <sup>0</sup> represents an adsorbed species. This model fitted measurements made with a laboratory-scale fluidised bed burning synthetic MSW during a 60 min test. It was also successful in predicting emissions between the secondary combustion chambers and the inlets to the air pollution control devices of two incinerators, when the surface coverage of active sites on the ash was suitably adjusted.

Altwicker [172] proceeded to extend the model to include superactive sites, using a similar four-stage process. Although the fraction of active sites is considered constant for normal sites, the concentration of superactive sites diminished exponentially with time due to accelerated destruction as well as formation. The resulting simulation gave rates of the correct magnitude  $\approx 1000 \text{ ng g}^{-1} \text{ s}^{-1}$  over a period of a few seconds. In assuming a standard temperature-distance profile for incinerators, Penner et al. [177] did not distinguish between hetero- and homogeneous reactions. In fact only surface reactions were included in their model. They then wrote rate expressions for an overall I-TEQ concentration in the gas and solid phases based on two intermediate variables. Q quantified the rate of I-TEQ formation on the particles' surface, and P the rate of transfer of precursor from the surface due to its adsorption, and the desorption of product I-TEQ. A number of extra variables had to be evaluated, including the extent of surface coverage, etc. Penner et al. [177] fitted the reaction parameters to make the solution fit the formation rates measured experimentally during 2 h of annealing flyash by Vogg and Stieglitz [146]. It was emphasized [177] that the model fitted both short- and long-term experiments. A sensitivity study was carried out for some of the inputs. Since the predicted I-TEQ output was proportional to the square of the precursor concentration, the result is very sensitive to the information inputted.

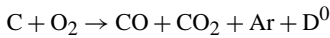
Huang and Buekens [89] have developed a model for the catalysed formation of dioxins from chlorophenols, by incorporating reversible adsorption from the gas phase, followed by reaction as follows,



where s is the solid. They found that the kinetics for each process were similar for three different precursors, 246TCP, 2346TeCP, and PeCP, using experimental data taken from different sources. The rate was found to be proportional to the concentration of precursor P at high concentrations, but to be second order at low concentrations. The model successfully predicted the low-temperature experimental data of Milligan and Altwicker [176]. The output was found to be sensitive to the number of active sites, which was assumed to be constant. However, Milligan and Altwicker [93] reported that the number of occupied sites falls as the temperature rises. This may partly explain why significant formation is predicted at temperatures around 600 °C [89], which is not found in practice. When likely concentrations of precursor in an incinerator are substituted into the model, the

predicted rates are so much smaller than those experimentally measured that Huang and Buekens concluded [89] that formation from precursors is negligible in MSW incinerators.

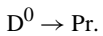
Huang and Buekens [192] followed this with a complementary model for de novo synthesis. This scheme relies on a general oxidation reaction for carbon with adsorbed PCDD/F as by-products,



followed by



or



They fitted four empirical rate constants for the different reactions by simulating some laboratory annealing tests, using an order for the oxygen reaction of 0.52. The kinetics were then successfully applied to predicting the performance of operating incinerators, but only when the flyash was held for periods of 5 or 10 min. In this case the kinetics were not adequate to explain reactions over short residence times.

The four alternative models of Gullett et al. [72] are statistical fits to the data set from their de novo entrainment experiments on MSW ash at low temperatures without precursors. The significant variables in each model vary slightly, but the major ones are the concentrations of O<sub>2</sub>, HCl, Cl<sub>2</sub>, the temperature, residence time, quench rate, and the quantity of Ca(OH)<sub>2</sub> added. The predictive capacity of the models was good, but the authors considered that the model may apply only to the conditions used in their tests.

Shin et al. [5] have carried out general process modeling to simulate 10 incinerators burning Korean MSW, concentrating on events in the low-temperature end. They first examined experimental data and concluded that there exists a maximum in the rate of formation of PCCD/F in the region of 400 °C. An empirical fit of this rate data was utilised for the input load to the gas-cleaning devices. They assumed that the flue gas conditions at the beginning of PCCD/F formation were identical for all incinerators, i.e., the concentrations of dust, precursors, and chlorine. The output concentrations of PCCD/F were determined by formation during cooling and the subsequent adsorption of the PCCD/F in the gas-cleaning system. The temperature regime and the type of downstream equipment, e.g., ESP, fabric filter and addition of activated carbon, determine the outcome. They claimed an overall *R*<sup>2</sup> correlation value of 0.987 between measured and predicted TEQ emissions from the 10

incinerators. A simple kinetic model for de novo formation was developed by Mätzing [193], involving the following variables: the carbon and copper contents of the ash, the surface area (BET) of the carbon, and the concentrations of oxygen and water vapour in the gas phase. Kinetic constants for the formation and destruction of PCDD/F were estimated from various annealing experiments. The model adequately described other experimental annealing results, but was inadequate for a cleaned flyash. In that case the temperature dependence was not well described, and the quantity of product was too low.

A model developed for the formation of both precursor and de novo dioxins has been based on the global surface area of the particles [171]. This approach assumed that a similar mechanism applied to both precursor and de novo routes, because of a limit to the availability of reactant when the reaction temperature rose. The rate of adsorption of gas-phase species on a surface can be estimated from kinetic theory [171,172], and applied both to precursor transfer and to HCl in the de novo route. The formation rate is determined by the reaction kinetics at lower temperatures, but is controlled by the diffusion rate of precursor at higher temperatures, typically above 300 °C [91]. This accounts for the maxima in PCDD/F product measured at around this temperature. The variables required for modeling are particle size distribution and the concentration of precursor in the gas phase. With de novo formation, the reaction rate between carbon and chlorine dominates at lower temperatures, but is limited by chlorine availability as the rate rises with temperature. Chlorine is then assumed to be supplied to the reaction via shuttling between the gas-phase HCl and the solid. Once again this leads to diffusional limitations at ~300 °C. For the de novo product to be predicted, the chlorine content of the fuel and the concentration of HCl in the gas are required.

A method for predicting the formation of PCDD/F on the ash of MSW incinerators by following their flow path has recently appeared [185]. Like Shin et al. [5] and Mätzing [193], the authors assumed that all ashes exhibit the same basic rates of formation with respect to temperature, i.e., with a normal distribution peaking at ~310 °C. The other variables chosen for inclusion were oxygen concentration, the carbon and copper contents of the ash, and its loading in the gas. A correlation for the removal of PCDD/F by addition of activated carbon was included. The model successfully predicted the concentrations of PCDD/F in the ash along the gas passages of two incinerators, but was restricted to the incineration of MSW in mass burn units.

### 5.3. Comments

The aim of PCDD/F models should be to produce algorithms suitable for CFD simulations. Great progress has been made recently in formulating models to describe homogeneous reactions, but these are still too specific to be applicable to the complex reaction network found in actual combustors. The emphasis on heterogeneous systems has produced a number of models which are based on measurements from laboratory tests. Some of them are limited to MSW incinerators [5,185] and only one can be regarded as universal [91]. All still require development and better verification.

### 6. Recommendations for further work

Both the homogeneous and heterogeneous formation reactions need further investigation. More experiments similar to those conducted in the gas phase by Sidhu et al. [51] with precursors other than PCPs are required to elucidate mechanisms, and to estimate their kinetics. The formation of furans needs more attention. Heterogeneous formation from precursors does not warrant further work, because the route seems to be a minor source of PCDD/F in industrial systems. The *de novo* route needs examination in connection with the participation of the solid surface. This should involve characterisation of the particle properties, including the distribution of the inherent carbon and the disposition of catalyst in relation to it. The interaction between gaseous and solid chlorine must be better understood. It is important to identify the conditions under which chlorine, carbon and oxygen can become limiting reactants. The relationship between the rate of carbon consumption and the rate of production of PCDD/F should be clarified.

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