Modeling the formation of PCDD/F in solid waste incinerators

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Abstract

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) appear in unacceptable amounts in the gaseous emissions during the incineration of wastes containing significant quantities of chlorine and metals, such as MSW and medical waste. They are formed both in the gas phase at temperatures above 600 °C and on the surface of the solid phase (flyash) in the temperature range 400–225 °C. Both the precursor (from existing smaller chlorinated molecules) and de novo (from elemental carbon) routes are involved. An empirically derived global model for their de novo formation on flyash in MSW and medical waste incinerators has now been extended to include the precursor mechanism, and a gas phase formation component, with separate rate expressions for PCDD and PCDF. Homogeneous PCDD formation is governed by the concentration of chlorophenols and PCDF by that of chlorophenols and chlorobenzenes. The result is a more complete system which distinguishes between the gas and solid phase contributions to the I-TEQ. An additional step for the adsorption of gaseous PCDD/F back onto the solid phase during cooling suggests this should be minimal in the gas ducts of an incinerator. The extended model has been tested against experimental data collected from a well-controlled pilot incinerator and commercial incinerators, and found to adequately describe the measured outputs. With the model it should be possible to predict the PCDD/F emissions from commercial incinerators, provided that the ash properties and the overall temperature–time profiles are known. © 2002 Published by Elsevier Science Ltd.

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1. Introduction

The reactions which lead to the formation of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) in incineration systems are many and varied (Choudry and Hutzinger, 1983; Gullett and Seeker, 1997). PCDD/F form pyrolytically in the gas phase at homogeneous reaction temperatures greater than 600 °C (Ballschmiter et al., 1985) and are thus found in the furnace exit plane of MSW incinerators (Düwel et al., 1990). In addition they form on flyash surfaces between 400 and 225 °C (heterogeneous reaction) from precursors such as chlorobenzenes and chlorophenols, and also by the de novo process from elemental carbon. For this reason the emission levels of PCDD/F depend strongly on the particulate emissions (Moyeda et al., 1990).

The ratio of gas phase to solid phase PCDD/F after the combustion stage depends on the conditions, specifically the period during which temperatures are maintained above 600 °C. For instance in an old incinerator which had no heat extraction but air addition to give a stack temperature of 550 °C (too high for heterogeneous reactions), the gas contained 2250 ng PCDD/FNm⁻³ (Stanmore and Clunies-Ross, 2000). In contrast, a modern incinerator with a secondary chamber temperature of 880 °C produced 80 ng PCDD/FNm⁻³ at the boiler outlet (Sakai et al., 2001).

Some ashes do not form PCDD/F e.g. coal ash. The reason is probably that suitable metals for catalysis of the chlorination reactions are not present (Altwicker,
Gulett et al. (1990) showed that copper is particularly effective, and was active in forming molecular chlorine by the Deacon reaction, as well promoting condensation and dechlorination. PCDD/F are destroyed on the ash by thermal decomposition and rapidly disappear above 400 °C (Vogg and Stieglitz, 1986).

There are different reaction pathways for PCDD and PCDF. The predominant pathway for PCDD formation is the condensation of chlorophenols (Tupperainen et al., 2000), whereas C$_1$ to Cl$_7$CDF generally form by progressive de-chlorination of higher homologues (Iino et al., 2000). Tests on model PAH compounds by Iino et al. (1999) demonstrated that chlorination causes the cleavage of C–C bonds in a coronene molecule. Oxygen concentrations below 2% lead to diminished formation rates for the de novo reaction, but values >2% make little difference (Gulett et al., 1990; Addink and Olie, 1995; Ryan and Altwicker, 2000).

Although the congener distributions are similar for most MSW combustion systems (Fiedler et al., 2000), it cannot be shown that the distribution is determined by thermodynamic equilibrium (Addink et al., 1998). The ratio of PCDD to PCDF is generally <0.3. Octachloro-DD is the most abundant congener in most samples from incinerators, but 2,3,4,7,8-pentachloroDF contributes most to the toxic equivalent I-TEQ (Fiedler et al., 2000).

The role of chlorine speciation in PCDD/F formation is still subject to debate. Inorganic chlorine alone will not form PCDD/F on the ash (Addink et al., 1998), whereas it was found that NaCl adsorbed onto clay was active in PCDD/F formation (Takasuga et al., 2000). Significant amounts of PCDD/F can be formed in the absence of gaseous chlorine if solid phase organic chlorine is present (Gulett et al., 1994). Experiments on the control of PCDD/F emissions in an operating MSW incinerator by addition of dolomite to the feed indicated that both PCDD and PCDF formation depended linearly on the HCl concentration (Takeshita and Akimoto, 1989).

As Milligan and Altwicker (1996a,b) showed that the precursor reaction follows a classical adsorption/reaction/desorption pathway, the adsorption kinetics and surface capacity of the ash becomes an important issue. There are many more active sites on the surface of ash than are occupied by PCDD/F at the usual surface concentrations found (Altwicker, 1996). Ryan and Altwicker (2000) were unable to correlate de novo PCDD/F yields with carbon surface area. The external surface area of the ash appears to be the appropriate surface for adsorption/reaction considerations (Stanmore, 2002).

Altwicker (1996) has produced a model of precursor formation based on adsorption, reaction and desorption. Two types of active site are proposed, one superactive at short times (s) and others which produce PCDD/F over a longer time scale. The model successfully predicts rates of formation of the correct order in operating incinerators at the superactive sites and in laboratory tests at the normal sites.

2. Modelling PCDD/F formation

At this time it is impossible to construct a fundamental model based on thermodynamics and reaction kinetics. Shaub and Tsang (1983) made some progress in this direction, with the rates determined by analogy to similar reactions. Their model served to set boundaries to the likely formation rates, and was constructed to favour PCDD/F formation. Any current model will need to be empirical, and will be unable to distinguish between congeners. The author has developed such a model, which incorporates both homogeneous and heterogeneous reactions.

2.1. Heterogeneous reaction

It has been calculated that there are approximately 2 × 10$^{18}$ active sites per gram of ash (Altwicker, 1996), equivalent to 10$^{-5}$ mol g$^{-1}$ of ash. As the maximum loadings of PCDD/F reported in the literature are of the order of 10$^{-9}$ mol g$^{-1}$ (Gulett et al., 1994), saturation of the active sites cannot be a consideration. Altwicker explains the high rates achieved at short times (seconds) by proposing two kinds of active site, one "superactive". These may be present, but the development outlined here does not distinguish the mechanisms involved.

Heterogeneous formation may take the form of either a precursor or de novo reaction. Both pass through single ring compound intermediates, but Stieglitz et al. (1997) have shown that single ring compounds are not precursors for PCB. The reactions are therefore treated separately, beginning with the de novo route.

A gas/surface reaction will be driven by the gas molecules which from kinetic considerations will impinge on a surface such as that of a flyash particle at a rate given by

$$r_{ads} = \frac{P}{\sqrt{2\pi MRT}} \text{ mol m}^{-2} \text{s}^{-1}$$

(1)

where $P$ is the partial pressure of the adsorbent, $M$ is the molecular mass of the adsorbent, $R$ is the gas constant and $T$ is the absolute temperature. The frequency of such an impinging molecule being retained (adsorbed) and then reacting can be included by means of a sticking factor $\alpha$. Then the rate of reaction is

$$\frac{dm_{PCDD/F}}{dt} = \frac{\alpha P}{\sqrt{2\pi MRT}} \text{ mol m}^{-2} \text{s}^{-1}$$

(2)

This formulation assumes that the rate of reaction is sufficiently to involve all the adsorbed molecules i.e. mass transfer controlled.
A single step process has been proposed by the author (Stanmore and Clunies-Ross, 2000) involving this probabilistic approach with a sticking factor. Its adoption was prompted by the experimental observation in a pilot incinerator that the rate of formation was proportional to the residence time in the 400–225 °C temperature range if it was limited by some form of mass transport. If the reaction was kinetically controlled, the rate would be influenced more strongly by temperature.

The rate for short times i.e. in-flight reactions was therefore assumed to be determined by the probability of a gas molecule striking one of the active sites, being captured and then reacting to form PCDD/F. The de novo model assumes that the reaction is driven by the chloride (HCl) concentration. It has been shown that molecular chlorine is the active chlorinating agent in forming de novo PCDD/F in an entrained flow reactor Wikström et al. (2001). Its concentration is determined by the gas phase chloride concentration (HCl) and the combustion conditions i.e. temperature and stoichiometry.

The literature on the influence of HCl concentration is contradictory, which may reflect the catalytic properties of different ashes and the combustion conditions. The rate of the Deacon reaction is directly proportional to the HCl concentration. It has been shown that molecular chlorine is the active chlorinating agent in forming de novo PCDD/F (Stanmore and Clunies-Ross, 2000). Its concentration is determined in terms of HCl molecule, and the second is a thermal destruction rate which is proportional to the surface concentration of PCDD/F. If desired, the expression can be reformulated in terms of $dT$ by introducing the cooling rate $\beta$ (K s$^{-1}$).

The first term in Eq. (3) is Eq. (2) specified for the HCl molecule, and the second is a thermal destruction rate which is proportional to the surface concentration of PCDD/F. If desired, the expression can be reformulated in terms of $d\frac{d_{PCDD/F}}{dT}$ by introducing the cooling rate $\beta$ (K s$^{-1}$).

In this approach, dioxins and furans are lumped together, although it has been shown that they form from carbon via different pathways (Stieglitz et al., 1997). All reactions are assumed to take place on the flyash surface. The value of $\alpha$ was found to be around $2 \times 10^{-9}$ for operating incinerators (Stanmore and Clunies-Ross, 2000). The value of $\alpha$ is sensitive to the concentration of sulphur in the system as shown in Fig. 1. This figure represents the data from pilot scale tests by Stanmore.

The resulting expression for the rate of formation of PCDD/F is (Stanmore and Clunies-Ross, 2000)

$$
\frac{d\text{mass}_{PCDD/F}}{dt} = \frac{0.38 \times 10^9 C_{\text{ash}}}{\rho d} \left[ \frac{0.72 nP}{\sqrt{T}} - 3.78 \times 10^{13} \times \exp \left( \frac{-20000}{T} \right) \right] X_p \text{ng}_{PCDD/F} \text{Nm}^{-3} \text{s}^{-1}
$$

(3)

where $P$ is the partial pressure of HCl (Pa), $T$ is the temperature (K), $X_p$ is the surface concentration of PCDD/F (mol m$^{-2}$), $C_{\text{ash}}$ the ash concentration (g m$^{-3}$), $\rho$ the particle density (kg m$^{-3}$) and $d$ the mean ($d_{1/2}$) diameter (m).

The major input to the de novo model is the time/temperature history of the gas flow and the concentration and the mean particle size of the ash. The assumptions of the de novo model are as follows:

1. PCDD/F is formed on the surface of the flyash particles (Stanmore, 2002), which are spherical. The surface area of the ash can be calculated from $A_t = \frac{4}{d} \text{m}^2 \text{g}^{-1}$, where $d$ is the particle diameter in microns and the ash density is assumed to be 2000 kg m$^{-3}$.

2. The reaction requires gaseous HCl to supply chlorine either directly to the reaction, or to metal chlorides on the ash which “shuttle” chlorine to the reaction site.

3. The formation rate is determined by the frequency with which HCl molecules impact on reaction sites.

4. The formation and destruction reactions are competitive.

5. For a given ash, the density of reaction sites is independent of particle origin and size (Stanmore, 2002).
and Clunies-Ross (2000) using fuel oil with different sulphur contents. The correlation line shown in Fig. 2 has the form

$$\alpha = 13.6 \times 10^{-9} \exp(-0.011C_{SO_2})$$

(4)

where $C_{SO_2}$ is the concentration of sulphur dioxide in ppm.

Eq. (3) applies to higher temperatures in the 225–400 °C range where mass transfer limits the formation rates. Another expression is needed to define the low temperature region where reaction and not diffusion is the controlling mechanism. In practice, this reaction rate will be strongly dependent on the ash surface and the availability of metals for catalysis. Stieglitz et al., 1993 have shown that the rate of de novo PCDD/F formation is proportional to the rate of carbon oxidation. Copper was found to be the only common metal with significant catalytic ability to form de novo PCDD/F (Stieglitz et al., 1989).

The catalytic effect of copper on carbon oxidation at low temperature has been examined by McKee (1970); Baker (1986) and de Soete (1988) with reported activation energies ranging between 79 and 94 kJ mol$^{-1}$. The activation energy for PCDD/F formation should therefore be of this order. The pre-exponential factor is unknown because the characteristic time for the reaction is much shorter than the test periods of hours conventionally used for reaction experiments e.g. Stieglitz et al. (1989). The formation reported by Stieglitz et al. at 300 °C reaches a constant value which is independent of carbon concentration. Assuming that the amounts so formed appear in 15 min, the rate at 300 °C can be taken as 15 ng g$^{-1}$ s$^{-1}$.

The reactions to form organics take place on the carbon surface but no correlation with carbon surface area is apparent (Stieglitz et al., 1990). To reflect the actual formation process (Stanmore, 2002), it is necessary to express the rate on the basis of particle area. With an activation energy of 87 kJ mol$^{-1}$ and a particle surface area of 0.025 m$^2$ g$^{-1}$ the overall rate expression for de novo PCDD/F formation from Stieglitz’s data becomes

$$\frac{dm_{PCDD/F}}{dt} = 0.3 \exp(-10500/T) \text{ mol m}^{-2}\text{s}^{-1}$$

(5)

Fig. 2 depicts some outputs from Eqs. (3) and (5) of rate against temperature for a number of scenarios in terms of available surface area of the ash $A_r$ and the partial pressure of HCl. The formation rate is fixed by whichever value of Eqs. (3) and (5) is the less. The three cases depict typical conditions for the cooling section of a MSW incinerator with $\alpha = 2 \times 10^{-9}$. The component curves of the process for Case 1, i.e. adsorption, reaction and destruction are detailed. The model reproduces the general shape of the bell-shaped curves found in the literature, and a pronounced effect due to particle size is evident. The maximum value of around 100 ng g$^{-1}$ s$^{-1}$ is typical of the average rate of formation found in incinerators (Altwicker, 1996).

The heterogeneous formation of PCDD/F from precursors proceeds in the absence of chlorine and even of oxygen, although oxygen increases the rate. Formation will proceed via adsorption of the gas phase precursors onto the ash surface as for the de novo process, followed by a condensation reaction. It was found (Hell et al., 2000) that the yield of PCDD and PCDF from isothermal tests at 300 °C with 2,3,6-trichlorophenol (TCP) were slightly S-shaped with respect to the inlet concentration of TCP.

In the mass transfer control region, the adsorption/reaction rate can be described by Eq. (2) using the properties and concentration of the appropriate precursors. There is little experimental information available specifically for rates of adsorption, but estimates have been made (Stanmore, 2002). Rghei and Eiceman (1982) passed TeCDD in the gas phase over a heated bed of flyash and measured the uptake. Takeup increased slightly with temperature between 100 and 300 °C and was complete in less than 2 hrs. Using the same sticking factor approach as in the solid phase model, the value of $\alpha$ was estimated to be $\sim 2 \times 10^{-6}$. The value estimated from the experiments of Milligan and Altwicker (1996b) for the TeCP molecule is $3 \times 10^{-6}$. Both of these results are orders of magnitude higher than $\alpha$ for the de novo reaction with HCl. This is not surprising as HCl is not the active de novo agent, but Cl which may represent <1% of the gaseous chlorine present. Also,
more active sites are probably involved in simple adsorption than in adsorption coupled with reaction.

This approach can be used to interpret experimental results such as those of Altwicker (1996), where TeCP in helium and 10% oxygen was passed over beds of flyash in the temperature range 250–400 °C. With a bed of 1 g of ash, over 95% of the PCDD formed was held on the bed. When the bed consisted of 0.1 g of ash diluted with 0.9 g of inert glass beads, the maximum specific rate was about 10 times higher. In the latter case, most of the PCDD formed was found in the cold trap. The results are reproduced in Fig. 3.

The particles in the diluted bed can be regarded as independent of the others and the reaction simulates entrainment flow conditions. The reaction rates reported for this case can be interpreted as kinetic-controlled at low temperatures, but diffusion-controlled at higher temperatures. The line marked Eq. (6) is an empirical fit to the points up to 350 °C.

\[
\frac{d\text{m}_{\text{PCDD/F}}}{dt} = 0.22 \exp(-10500/T)\text{[ClPh]} \text{ mol m}^{-2} \text{s}^{-1}
\]

(6)

where [ClPh] is the gas phase concentration of chlorophenols in terms of partial pressure (Pa). The results of Hell et al. (2000) indicate the the reaction is first order with respect to chlorophenol at low concentrations.

The activation energy in Eq. (6) is 87 kJ mol\(^{-1}\), which is lower than the value of 101 kJ mol\(^{-1}\) given by Shaub and Tsang (1983) for the homogeneous condensation reaction of chlorophenol. However decreases in activation energy of this order of magnitude are common for catalysed reactions (Walas, 1989). The activation energy is the same as for the copper-catalysed oxidation of carbon which was assumed for the de novo reaction.

The decline in reaction rate with temperature above 350 °C in Fig. 3 could be due to a combination of the thermal decomposition of the product and the lack of sufficient reactant molecules to the surface. Application of the destruction kinetics contained in Eq. (3) suggests that the rate of this reaction at 350 °C is insufficient to explain the rate maximum in the data. Application of Eq. (2) to TeCP gives the expression

\[
\frac{d\text{m}_{\text{PCDD/F}}}{dt} = 0.51 \frac{zP}{\sqrt{T}} \text{ mol m}^{-2} \text{s}^{-1}
\]

(7)

If the value of \(z\) is fixed at 0.35 × 10\(^{-6}\), the line marked Eq. (7) results. This factor is less by an order of magnitude than the \(z\) values estimated for simple adsorption. The difference can be explained by the need to incorporate reaction probability into the process. Milligan and Altwicker (1996a) report conversion values of TeCP to PCDD of about 4% under these conditions.

It is proposed that the precursor reaction rates can be estimated by use of either Eq. (6) or Eq. (7), whichever gives the lower value, together with the destruction expression contained in Eq. (3). The results for formation rate as a function of temperature are similar to those for the de novo reaction as given in Fig. 2, but of a different magnitude.

The expression for the rate of formation of PCDD on ash from precursors i.e. Eq. (6) can be checked against two independent laboratory results. Altwicker and Milligan (1993) measured formation at 300 °C from gas phase 2,3,4,6-TeCP at a concentration of 400 ng ml\(^{-1}\) (2.24 Pa). Their MSW flyash was screened to be <210 μm, so a mean particle size of 120 μm is reasonable. They found a rate of 4.4 μg g\(^{-1}\) min\(^{-1}\), which is equivalent to 7.7 × 10\(^{-9}\) mol m\(^{-2}\) s\(^{-1}\). Eq. (6) gives a figure of 5.4 × 10\(^{-9}\) mol m\(^{-2}\) s\(^{-1}\) which must be considered good agreement. The second result from Hell et al. (2001) gives rate constants \(k\) at 300 °C for 2,4,6-TCP passed at various concentrations over two ashes, one obtained from the EPA and the other from Ontario. The value of \(k\) found for the former was \(1.7 \times 10^{-4}\) s\(^{-1}\) and for the latter was \(3.1 \times 10^{-3}\) s\(^{-1}\). With the assumption of a particle size of 120 μm, the predicted rate from Eq. (6) is \(1.2 \times 10^{-4}\) s\(^{-1}\).

The results suggest that an equation of the form of (6) is a satisfactory means of predicting PCDD formation from precursors, once the concentration of chlorophenols is known. A method of predicting the formation of PCDF from precursors is still unavailable.

The solid phase model described by Eqs. (3), (5) and (6) has now been extended to include an extra process, namely the adsorption of gas phase PCDD/F onto the flyash surface. An adsorption step based on Eq. (2) was incorporated as an extra term, but the rate is so slow.
that it makes very little difference to the partitioning of PCDD/F between the gas and solid. This is because the concentration of PCDD/F in the gas phase is much lower than that of HCl or precursors which drive the solid phase formation reactions, and destruction is catalysed by the ash surface.

As an example, if the gas phase concentration of PCDD/F is 200 ng N m$^{-3}$ i.e. a partial pressure of 1.2 × 10$^{-6}$ Pa, its adsorption rate at 300 °C is 0.5 × 10$^{-13}$ mol m$^{-2}$ s$^{-1}$. On 30 μm particles this is equivalent to 2 × 10$^{-3}$ ng g$^{-1}$ s$^{-1}$, an infinitesimal amount. Because of the nature of the temperature relationship in Eq. (2), the rate of adsorption is fairly insensitive to temperature change. However the partition coefficient will be more strongly affected (Altwicker, 1996) and will influence the final concentrations.

2.2. Homogeneous reaction

Laboratory results indicate that dioxin/furans should be rapidly destroyed in a well-mixed gas phase at temperatures above 700 °C (Gullett and Seeker, 1997), but they are consistently found in the flue gases of incinerators which have been sampled at temperatures higher than this. This could be due to the continuing presence of other (precursor) species, poor mixing ie bypassing of gas down the cooler walls or even a sampling artifact. Nevertheless, Ballschmiter et al. (1985) and Sidhu et al. (1995) showed that formation is possible at elevated temperatures.

Following Shaub and Tsang, it is assumed that formation and destruction reactions are in competition. It is difficult to get good data for setting up a model, as insufficient information is published. Gas phase formation from the pyrolytic destruction of 2,4,6-TCP for 2 s at temperatures up to 800 °C is reported by Sidhu et al. TCDD products persist up to 800 °C and are virtually unchanged in concentration between 700 and 800 °C. This makes them difficult to model simply, as a destruction reaction should cause a continuous fall in concentration as temperature rises. Sidhu et al. adopt a modified Shaub and Tsang scheme to get results of the correct magnitude.

It is clear that PCDD are formed predominantly from chlorophenols (ClPh). The statistical analyses of products, Wikström and Marklund (1998) and Tuppurainen et al. (2000) indicate that the formation of PCDD is strongly related to ClPh concentration. For the basic condensation reaction in the formation of PCDD, Shaub and Tsang give

$$\text{ClPh} + \text{ClPh}^* \rightarrow \text{POP} + \text{Cl} \quad E = 101000 \text{ kJ mol}^{-1}$$

where ClPh and ClPh$^*$ represent a chlorophenol molecule and radical respectively, and POP is a polychlorinated 2-phenoxyphenol. Since this is a well-established reaction, the value of 101 kJ mol$^{-1}$ was retained. The reaction suggests that the rate could be proportional to the concentration of ClPh to the second power, but a first power correlation fits their results better.

For formation processes, Wikström and Marklund (1998, 2000) and Wikström et al. (1999) give the most comprehensive information in the form of PCDD/F and precursor concentrations at the outlet of a pilot scale fluidised bed incinerator burning MSW at 850 °C. Interpretation of the results is made difficult because of some uncertainty about the temperature history of the gases. The correlation for PCDD then becomes

$$\frac{dm_{PCDD}}{dt} = 5.0 \times 10^8 \exp \left( - \frac{12150}{T} \right) \text{[ClPh]} \text{ ng}_D \text{ N m}^{-3} \text{ s}^{-1} \quad (8)$$

where [ClPh] is the concentration of bi- to penta-substituted chlorophenols, expressed in μg N m$^{-3}$.

As far as PCDF are concerned, the pilot scale data of Wikström et al. (1999) show no correlation between exit PCDF and either the ClPh or ClBz concentrations. However the correlation with the product of their concentrations [ClPh][ClBz] has an $R^2$ value of 0.8. Then a global model can be written for formation of PCDF as

$$\frac{dm_{PCDF}}{dt} = 1.2 \times 10^6 \exp \left( - \frac{12150}{T} \right) \text{[ClPh][ClBz]} \text{ ng}_f \text{ N m}^{-3} \text{ s}^{-1} \quad (9)$$

with the concentrations of chlorophenols and chlorobenzenes (excluding monochloro) expressed in μg N m$^{-3}$. Most of the high temperature PCDD/F is present as furans, and the above equations under typical conditions predict that three quarters of the high temperature PCDD/F are furans and one quarter is dioxins.

The best data for gas phase destruction under well-documented conditions available to the author were from tests before and after the second stage combustor (1.5 s at 1100 °C) of a hospital incinerator in New Zealand specifically to measure destruction under high temperatures (Abbott et al., 1989). The inlet gas came from a starved-air primary combustor operated at 700 °C. Since formation would be taking place simultaneously with destruction, the simple destruction rates calculated under these conditions of 3.2 s$^{-1}$ for PCDD and 2.0 s$^{-1}$ for PCDF must be corrected. Using Eqs. (8) and (9) to describe formation, with ClPh and ClBz concentrations taken as 100 μg N m$^{-3}$ and an activation energy of 330 kJ mol$^{-1}$ (following Shaub and Tsang), the kinetics of thermal destruction are
\[ r_{\text{dest}} = 3 \times 10^{13} \exp \left( -\frac{40000}{T} \right) \text{ s}^{-1} \] (10)

The destruction rate exceeds formation rates somewhere in the temperature range 800–900 °C, depending on concentrations. Little PCDD/F should be present for significant residence times at temperatures above this range. This is illustrated in Fig. 4 where the net rate (formation–destruction) is plotted against temperature for chlorophenol and chlorobenzene concentrations of 10 and 20 μg N m⁻³ respectively, and a PCDD/F concentration of 1000 ng N m⁻³.

The maximum value of ~50 ng N m⁻³ s⁻¹ should be compared with the output of the model of Shaub and Tsang (1983), which gives a maximum of about 90 ng N m⁻³ at 827 °C after 1 s of reaction involving 10% oxygen and a local excess of hydrocarbon. The experimental figures for TCDD formed from 6.87 × 10⁴ μg m⁻³ of TCP in 2 s are 11.3 μg m⁻³ at 700 °C and 9.9 μg m⁻³ at 800 °C. The present model i.e. Eqs. (8) and (10) predict 26 μg m⁻³ at 700 °C and 44 μg m⁻³ at 800 °C.

3. Application of the model

The approach described above pertains to the formation of PCDD/F in the furnace and heat exchanger sections of an incinerator. PCDD/F formation in both the gas and solid phases can be predicted. Eqs. (3)–(10) can be integrated with time, commencing at the highest temperature. The concentrations of the species formed are required for the destruction reactions, Eq. (3) on the ash and Eq. (8) in the gas phase. The integration is terminated when no further formation is predicted by Eqs. (5) and (6), which describe the de novo and precursor processes. Further PCDD/F reactions will occur—i.e. removal, in downstream gas cleaning devices. This effect has been successfully modeled by Shin et al. (1999). A complete description of PCDD/F formation processes in incineration systems is therefore available.

The homogeneous model is tested against measured values from the pilot fluidised bed incinerator in Fig. 5, with 20% error bars. The values for temperature profile, residence times, HCl concentration, ash loading etc. are taken from the Wikström references. The values are in effect replotted the data from which they were derived, but an independent value denoted “lab test” from Dickson et al. (1992) for PCDD formation from 2,3,6-trichlorophenol in a quartz reactor at 600 °C is well predicted.

Output from the extended model is compared in Fig. 6 with a measured value from a Korean incinerator burning 200 tonnes per day of MSW (Shin et al., 1999). The location for modelling and sampling is at the exit of the heat extraction process, before gas cleaning. A low intitial concentration was assumed on the solid phase, but this makes little difference to the integrated value. Although the temperature profiles were roughly known, other important variables had to be assumed, based on values obtained from similar incinerators. The values are listed in the caption to the figure. The ratio of PCDD/F mass to I-TEQ mass was taken to be 100 (Stanmore and Clunies-Ross, 2000).
As seen in Fig. 6, there is reasonable agreement between the measured and predicted outputs, but the result depends strongly on the assumed inputs. There is a steep rise in solid phase PCDD/F during the final stages of the cooling process in the heat exchanger. Further simulations on other incinerators in Shin’s paper are shown in Fig. 7, using the assumptions indicated. In general the values are adequately predicted, with 20% error bars.

References


