

# Formation of PCDD/F in municipal solid waste incinerators: laboratory and modeling studies

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## Abstract

Recent laboratory results on the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) are reviewed, with emphasis on heterogeneous, fly ash-mediated reactions. The well-studied de novo synthesis yields PCDD/PCDF ratios less than one, a value frequently found in municipal solid waste incinerators. Its apparent rate cannot, however, explain PCDD/F-formation in incinerators during flue gas residence times. Reactions of chlorophenols yield PCDD, either in the solid or gas phase, and are much faster, but generally lead to PCDD/PCDF  $\gg 1$  at comparable temperatures. PCDF-yields from chlorobenzenes are much lower under comparable conditions, but increase at higher temperatures. Different experimental combustion systems have proven that PCDD/F can form rapidly at rates comparable to apparent incinerator rates, i.e., formation during flue gas passage from the furnace through the air pollution control device.

The properties of fly ash play an important role in determining rates and yields, but there is at present hardly a quantitative link between fly ash physical/chemical properties and chemical reactivity. Some success has been achieved in applying a modified four-step model of PCDD-formation to incinerator data. The concept of active and superactive sites on fly ash is introduced, it may be useful in future experimental designs. For future control approaches that are not add-on oriented a better understanding of the time/temperature history of fly ash formation and the intrinsic kinetics of precursor reactions is required.

*Keywords:* Dioxins/Furans; Fly ash; De novo synthesis; Chlorophenols; Chlorobenzenes; Modeling PCDD/F formation; Time/temperature regimes

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## 1. Introduction

Informed speculation has no place in the archival literature.

A.R.

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Some years ago a paper submitted by this author was rejected by a journal; the rejection included the above comment by an A.R. (anonymous reviewer). I cite it here, because the topic of this contribution has invited much speculation, in print or otherwise, over the last two decades. The present contribution makes no claim to be free of speculation, informed or otherwise. Some of the seminal papers addressing the topic of formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) have dared to speculate, often successfully, on the relevance of laboratory and modeling studies to PCDD/F-formation and emissions in operating municipal solid waste incinerators (MSWIs).

Ever since the report by Olie et al. [1] that PCDD/F were present in MSWI-effluent streams, these compounds have attracted a number of investigators. Recently, all probable sources of PCDD/F and their formation have been reviewed [2]. Studies of PCDD/F-formation are difficult due to the low concentrations that are desirable in laboratory studies (both from a simulation and a toxicity point of view), the large number of congeners and isomers, and extensive sampling, cleanup, and analytical capabilities that must be employed to achieve quantitative results.

In a recent review article [3] this author summarized pertinent information on homogeneous and heterogeneous formation of PCDD/F, together with experimental designs employed. Table 5 in that paper gives an overview of the diversity of conditions that have been used by different investigators, together with apparent rates of PCDD/F-formation. Therefore, this review will emphasize primarily more recent results. Basically, two approaches are being used by laboratory investigators: a segmented and a system flow reactor approach. In the former a portion of the incinerator system (feed/furnace/sec. combustion chamber/boiler/air pollution control devices (APCD)/stack) is isolated on the basis of temperature, residence time, and potential PCDD/F-precursor(s) for laboratory simulation. Though many studies have been conducted using this approach, intrinsic chemical kinetics data is still largely missing for total PCDD/F, let alone individual congeners. In the system flow reactor approach, combustion gases may be present and the temperature may vary, while residence times are short. Specific precursors may or may not be present.

This review will address the nature of the precursors and time/temperature regimes, reaction time scales, fly ash properties, and modeling. The emphasis will be on heterogeneous, fly ash mediated reactions.

## 2. Precursors and time/temperature regimes

Precursors are conveniently classified into several categories, though the division between these categories is somewhat arbitrary. The choices made here are based on (1) formation from carbonaceous matrices within fly ash (*de novo*), (2) formation from chemically similar compounds, i.e., chlorobenzenes (CB), chlorophenols (CP), polychlorinated biphenyls (PCB), dioxin and furan, (3) routes to PCDF, (4) other C, H, O, Cl combinations (which may be classified as *de novo*), and (5) rapid formation/combustion intermediates.

### 3. De novo reactions

The most widely studied reaction for PCDD/F-formation is the so-called de novo reaction (formation from chemically dissimilar precursors; in the most restrictive sense, this refers to the carbonaceous matrix within the fly ash itself; however, precursors discussed in Section 6 may be classified as de novo. In fact, the true precursors within the carbonaceous matrix may not be dissimilar at all, see below). The de novo reaction yields PCDD/F when extracted fly ash is heated in a stream containing at least a few percent oxygen. The products remain largely on the fly ash; typical yields are  $10^2$ – $10^3$  ng PCDD/F/g fly ash (total tetra- through octa-PCDD/F congeners). For most MSWI-fly ashes these products are characterized by a PCDD/PCDF ratio that is less than one and congener distributions that resemble closely those found originally on the fly ash as obtained from the incinerator. De novo rates generally fall in the range  $10^{-4}$ – $10^{-1}$   $\mu\text{g}$  PCDD/F/g fly ash/min though a few higher values can be calculated from published data. The dependence on oxygen concentration is not firmly established, but appears to be of order 0.5. In the absence of oxygen, the reaction rate, though much slower, is not zero, suggesting that oxygen donors may be present in the fly ash.

The temperature dependence of the de novo reaction is plotted in Fig. 1 for three MSWI-fly ashes. For comparison a coal fly ash is shown, which produced no measurable PCDD/F [4]. The temperature window does not exactly coincide with the typical operating temperatures of ESPs in MSWIs, for which the de novo reaction is often cited as the explanation.

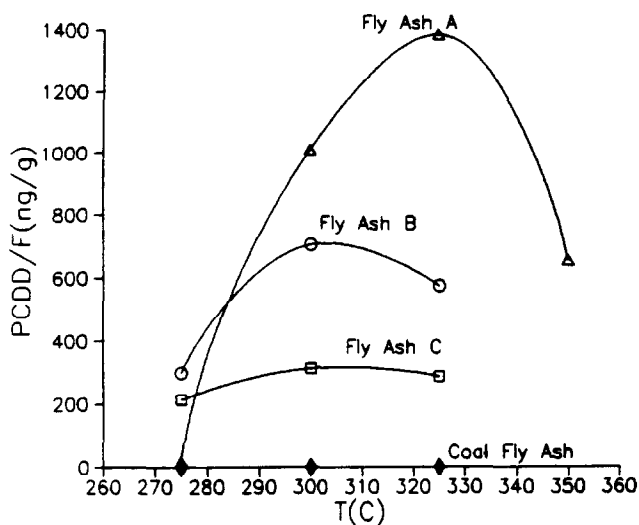


Fig. 1. PCDD/F-yields vs. temperature from de novo synthesis for three MSWI-fly ashes and one coal fly ash in 30 min, 10% O<sub>2</sub>, at 80 ml/min.

The mechanism of the de novo reaction has been widely discussed, especially by Stieglitz and coworkers [5–12], who proposed copper as a catalyst (other transition metal salts have also been proposed) and also worked with a ‘model fly ash’. Hagenmaier et al. [13] provided evidence for the Deacon reaction as a mechanism. Invoking this reaction lends itself to an interpretation of the role of both copper and chlorine, the latter (or Cl radicals) serving to cleave pre-existing aromatic structures in the carbonaceous matrix followed by chlorination/dechlorination. Dioxin and furan structures have been postulated to be present in a variety of coals and other organic carbon structures.

Most recently, Stieglitz and coworkers [14] provided evidence from scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) investigations showing that fly ash contains a priori 400–800  $\mu\text{g/g}$  organic chlorine bound to the carbon structures in fly ash. In model mixtures it was shown that the transfer of inorganic chloride (from KCl) produced C–Cl bonds in a process catalyzed by  $\text{Cu}^{2+}$ . The subsequent oxidation to form PCDD/F, CB, and CP is thought to be the rate-determining step. This evidence goes a long way towards explaining the nature of the participation of inorganic chlorides in the formation of organochlorine compounds.

In seeking further mechanistic information on this reaction, we explored carbon gasification and PCDD/F-synthesis from  $^{13}\text{C}$ -carbon. Low temperature C-gasification in the presence of oxygen has been shown to occur with various carbons [15], including the carbon in fly ash [4, 12]; yielding CO and  $\text{CO}_2$ . Mechanisms of C-gasification have been discussed extensively in the literature [16, 17]. Formation of carbon–oxygen complexes, including bound CO, has been postulated. Coflowing  $^{13}\text{C}$ -CO or  $^{13}\text{C}$ - $\text{CO}_2$  with 10% oxygen over fly ash for 30 min at 300°C gave no evidence of label incorporation into the PCDD/F-moieties; one may conclude that CO and  $\text{CO}_2$  are not precursors to PCDD/F in the de novo reaction.

When amorphous  $^{13}\text{C}$ -carbon was physically mixed with a fly ash and a typical de novo run conducted, no  $^{13}\text{C}$ -PCDD/F were detected; only  $^{12}\text{C}$ -labeled products were formed. However, when amorphous  $^{13}\text{C}$ -carbon was activated, or an activated, labeled C was used, both  $^{13}\text{C}$ - and  $^{12}\text{C}$ -PCDD/F were observed but no PCDD/F containing both  $^{12}\text{C}$  and  $^{13}\text{C}$ . This result is further support that pre-existing aromatic structures are present in activated carbons and that the Cl-source must be in the fly ash, when gas-phase chlorine species are absent in the entering gas stream [18].

Different fly ashes show different rates of carbon-gasification and PCDD/F-formation via the de novo reaction, Table 1. These reactions appear to occur in parallel, but may have site activation in common. The different rates of de novo PCDD/F-formation from different fly ashes suggest that knowledge of the nature of the carbonaceous matrix in fly ash and control over its formation (it appears to be more of a question of the type of carbon, rather than the quantity) would be important in assessing PCDD/F-formation potential. Though experimental results of Stieglitz et al. [10, 11] indicated no effect of carbon type on yield in a model fly ash doped with different types of carbon, more recent results [19] suggest that an increase in chemisorbed oxygen on activated carbons decreases the formation of organohalogen

Table 1

A comparison of carbon gasification with de novo synthesis results (Fly ash 1 is a coal fly ash; 2–5 are MSWI-fly ashes)

| Fly ash | % C  | Rate <sup>a</sup> | CO <sub>2</sub> /CO | ΣCB <sup>b</sup> | ΣCP <sup>b</sup> | PCDD/F <sup>b</sup> |
|---------|------|-------------------|---------------------|------------------|------------------|---------------------|
| 1       | 3.7  | 0.022             | 6                   | 2.5              | ND               | ND                  |
| 2       | ~1.3 | 0.24              | 11                  | 1625             | NA               | < 200               |
| 3       | 1.95 | 0.96              | 8.5                 | 2900             | 19               | 316                 |
| 4       | 1.85 | 0.83              | 13                  | 5700             | 290              | 705                 |
| 5       | 7.4  | 4.5               | 17                  | 13900            | 1370             | 1010                |

<sup>a</sup> mg C g<sup>-1</sup> min<sup>-1</sup>.

<sup>b</sup> ng g<sup>-1</sup>; 300 °C/30 min.

ND = not detected.

NA = not analyzed.

compounds, whereas different degrees of carbon activities lead to different PCDD/F-yields (an untreated activated carbon gave the highest yield). A recent study [20] showed the strong influence of Cu concentration on the PCDD/PCDF-ratio, which was found to be 33 (0.1% CuCl<sub>2</sub>) and 0.2 (5% CuCl<sub>2</sub>).

There can be little doubt that the de novo reactions are important contributors to PCDD/F in fly ash at moderate temperatures over long times.

#### 4. Chemical similar precursors

In this section we will first discuss the two most obvious precursor types, namely chlorobenzenes (CBs) and chlorophenols (CPs). Although these reactions are not limited to the low temperature window of the de novo reaction, it is convenient to discuss them first from that perspective.

##### 4.1. Chlorobenzene

Stieglitz et al. [7] were the first to report the generation of chlorobenzenes (CBs) from the de novo reaction forming PCDD/F. This raises the question whether CBs are yet another parallel reaction product or are intermediates to PCDD/F. There is also evidence from high(er) temperature oxidation studies (combustion and noncombustion mode) that chlorobenzenes, such as dichlorobenzenes, form PCDD/F. In addition, 1,2-dichlorobenzene is a commonly detected product in waste combustion.

When 1,2,-dichlorobenzene (60–700 mg/ml) was coflowed with air over fly ash at 300 °C, there was no evidence of a shift in the typical de novo congener distribution when compared to experiments that contained no dichlorobenzene, but yields were reduced, with PCDF-yields declining more than PCDD-yields. One caveat for this type of experiment is the fact that only tetra–octa congeners were analyzed, whereas it is plausible that di–tri congeners might be the expected PCDD/F. Labeled <sup>13</sup>C-1,4-dichlorobenzene gave no evidence of label incorporation [21].

In experiments with 1,2,4,5-tetrachlorobenzene (10% O<sub>2</sub>, 300 °C) higher chlorobenzenes, principally pentachlorobenzene, and chlorophenols, principally tetrachlorophenol, were formed, as well as PCDD/F; typical PCDD/PCDF ratios were 20–40; rates of PCDD formation ranged in 0.20–0.45 µg/g min, while rates of PCDF-formation ranged in 0.0047–0.017 µg/g min [22]. Here also yields declined, except for H<sub>6</sub>CDD–OCDD which increased dramatically. Ross et al. [23] formed predominantly PCDD from reactions of T<sub>4</sub>CB over fly ash; the yield in O<sub>2</sub> was 9 × the yield in N<sub>2</sub>. When compared to results obtained with chlorophenols (CB) (see below) the body of evidence suggests that CBs are far less reactive precursors.

In Section 5 some results from high(er) temperature reactions involving chlorobenzenes are discussed.

#### 4.2. Chlorophenols

These reactions were pioneered by Karasek and Dickson [24–26] who showed conclusively, using <sup>13</sup>C-labeled pentachlorophenol, that PCDD formed in a temperature window comparable to the de novo window and that fly ash promoted the reaction; other substances, such as fire brick were inert (OCDD only was observed over fire brick in much lower yield).

Our studies with chlorophenols and fly ash were motivated by the continuing need to learn more about the kinetics of these reactions as well as an interest in the relative reactivity of chlorophenols. In a preliminary investigation it was determined that 2,3,4,6-tetrachlorophenol formed PCDD more rapidly, and thus permitting shorter reaction times, than either pentachlorophenol or trichlorophenols. Therefore, this phenol became the precursor of choice for subsequent studies.

Fig. 2 summarizes a large number of experiments on a plot of PCDD-formation rate, µg/g min, against temperature, with reaction times of 2–120 min. The lower curve 1 resulted when 1.0 g fly ash was used in the fixed-bed reactor; a peak in rate occurred at about 325 °C, most of the PCDD (>95%) was found on the fly ash. When only 0.1 g fly ash was used (plus 0.9 g inert glass beads) the upper curve 2 resulted. Thus, PCDD was formed much more rapidly, but most of it was now found in the downstream cold trap, i.e., it had entered the gas phase. This result indicates the fundamental importance of the precursor/fly ash ratio in studying and interpreting heterogeneous PCDD/F-formation mechanisms. The distinguishing feature of running the reaction in this fashion is the differential mode, i.e., inlet T<sub>4</sub>CP ≅ outlet T<sub>4</sub>CP, thus enabling the acquisition of true kinetic data.

Different fly ashes gave different rates of PCDD-formation. The maximum rate observed (T<sub>4</sub>CP 350 ng/ml, 0.1 g fly ash, 10% O<sub>2</sub>, 300 °C) was 13.4 µg/g min. Even a coal fly ash gave a measurable rate, unlike under de novo conditions only. The other distinguishing features of these reactions are the dominance of the hexachloro congeners and the virtual absence of PCDF (*t* < 5 min, no PCDF can be detected; later, PCDF are formed comparable to de novo yields and congener patterns).

Because the chlorophenol yields a distinct congener pattern, the results can also be used to calculate relative yields between the chlorophenol precursor synthesis and the de novo synthesis. An example is given in Table 2. Similar conclusions were reached

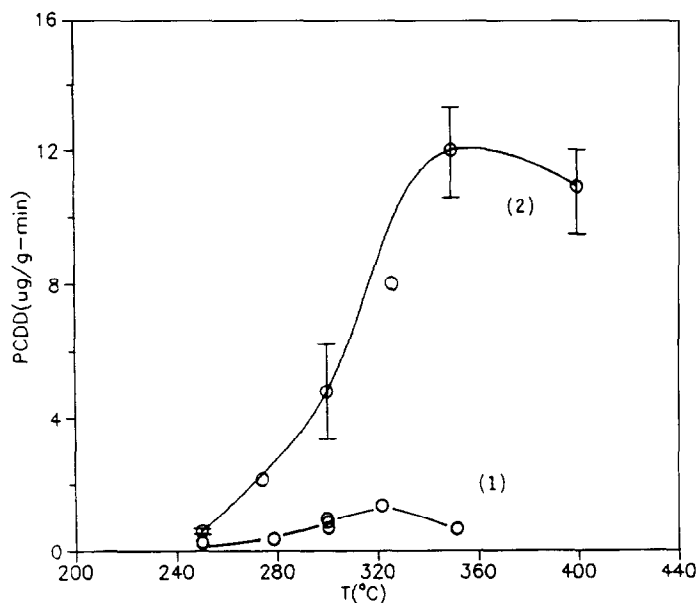


Fig. 2. PCDD-formation rates,  $\mu\text{g/g min}$ , from 2,3,4,6- $\text{T}_4\text{CP}$  vs. temperature, reaction times 2–120 min,  $\text{T}_4\text{CP} = 350\text{--}400\text{ ng/ml}$ , 10%  $\text{O}_2$  at 80 ml/min. Lower curve (1): 1.0 g fly ash, upper curve (2): 0.1 g fly ash plus 0.9 g glass beads.

Table 2  
De novo synthesis vs. tetrachlorophenol precursor

| Fly ash                       | 4       | 6       |
|-------------------------------|---------|---------|
| de novo                       | 705 ng  | 48 ng   |
| $P_g = \text{T}_4\text{CP}^b$ | 6100 ng | 6000 ng |

<sup>a</sup>  $T = 300\text{ }^\circ\text{C}$ ,  $t = 30\text{ min}$ , fly ash = 1.00 g.

<sup>b</sup>  $T = 300\text{ }^\circ\text{C}$ ,  $t = 15\text{ min}$ , fly ash = 0.10 g,  $\text{T}_4\text{CP} = 400\text{ ng/ml}$ .

by Dickson et al. [27], who used  $^{13}\text{C}$ -pentachlorophenol with a mixture of silica and activated carbon, in the presence and absence of  $\text{CuCl}_2$ .

The results from these breakthrough experiments suggest a 'classic' catalytic reaction: adsorption of reactant ( $\text{T}_4\text{CP}$ ) on a catalytic site, surface reaction to product (PCDD), desorption of product, and adsorption of another reactant molecule. To understand PCDD-formation reaction from gas-phase precursors classical catalytic reaction models such as the Langmuir–Hinshelwood (L–H) and Eley–Rideal (E–R) mechanisms are used. In the following analysis it is assumed that external and internal mass transfer resistances are negligible. Theoretical calculations [28] suggest that external mass transfer limitations are not important during precursor/fly ash reactions under post-combustion incinerator conditions simulated in our experiments,

i.e., the transport time scale for precursor molecules to the fly ash surface is much shorter than the reaction time scale. Fly ash surface areas are low [29, 30] when compared to typical heterogeneous catalysts, suggesting that a significant pore structure is not present; accordingly, internal mass transfer limitations may also not be important.

Modeling studies in our laboratory [25, 31] and by Shaub and Tsang [32] have assumed an Eley–Rideal mechanism, although this assumption has never been tested experimentally. Assume that chlorophenol adsorbs nondissociatively on catalytic sites in fly ash, is followed by reaction to PCDD, desorption of PCDD, and re-adsorption of chlorophenol, as well as adsorption/desorption equilibrium of the chlorophenol.

In the Langmuir–Hinshelwood model two adjacent, adsorbed molecules react, followed by desorption of product [33]:



where  $P_s$  is an adsorbed chlorophenol precursor molecule,  $D_s$  is an adsorbed PCDD product molecule, and  $D_g$  is a desorbed gas-phase product molecule. One can write an apparent PCDD-formation rate equation as

$$r_{\text{LH}} = k_{\text{LH}} P_s^2 \quad (3)$$

where  $k_{\text{LH}}$  is the Langmuir–Hinshelwood rate constant. Defining the fractional surface coverage as

$$\theta_s = \frac{P_s}{N_m} \quad (4)$$

where  $N_m$  is the total number of adsorption sites per unit mass of fly ash results in the final expression for the Langmuir–Hinshelwood mechanism

$$r_{\text{LH}} = k_{\text{LH}} N_m^2 \theta_s^2 \quad (5)$$

or

$$r_{\text{LH}} = k'_{\text{LH}} \theta_s^2 \quad (6)$$

The Eley–Rideal model assumes that an adsorbed reactant molecule reacts instead with an impinging gas-phase reactant molecule, followed by desorption of the product molecule



The rate expression for the Eley–Rideal mechanism can then be written as

$$r_{\text{ER}} = k_{\text{ER}} P_s P_g = k_{\text{ER}} N_m \theta_s P_g \quad (9)$$



or

$$r_{ER} = k'_{ER} \theta_s P_g \quad (10)$$

Three of the parameters present in the above expressions can be measured directly: the rate of reaction,  $r_{LH}$  or  $r_{ER}$ ; the gas-phase precursor concentration,  $P_g$ ; and the solid-phase precursor concentration,  $P_s$ . One needs to estimate the total number of adsorption sites per gram of fly ash,  $N_m$ , and thus calculate the surface coverage  $\theta_s$ . In many chemisorption systems, the binding energy is high enough that the surface coverage is about unity near room temperature even at low gas-phase pressures [31]. If true for the chlorophenol/fly ash system, one can measure  $N_m$ , and thus surface coverages over a wide range of concentrations and temperatures.

Therefore, a series of adsorption experiments using  $T_4CP$  in helium were run at three different gas-phase concentrations (65–725 mg/ml) and temperatures ranging from 100 to 400 °C. For each run,  $T_4CP$  flowed through 0.10 g of fly ash mixed with 0.90 g inactive glass beads for at least 30 min. Breakthrough was observed after a few minutes by condensation of chlorophenols in the cool inlet tube of the impinger trap connected to the outlet of the reactor. GC/MS analysis of the fly ash extract resulted in the total amount of  $T_4CP$  adsorbed to the fly ash. By dividing these totals by the molecular weight and assuming that one molecule occupied one site, the total number of sites occupied per gram of fly ash was calculated.

Fig. 3 is a plot of the total surface coverage by  $T_4CP$  as a function of gas-phase concentration and temperature. At a temperature of 100 °C, the total surface coverage

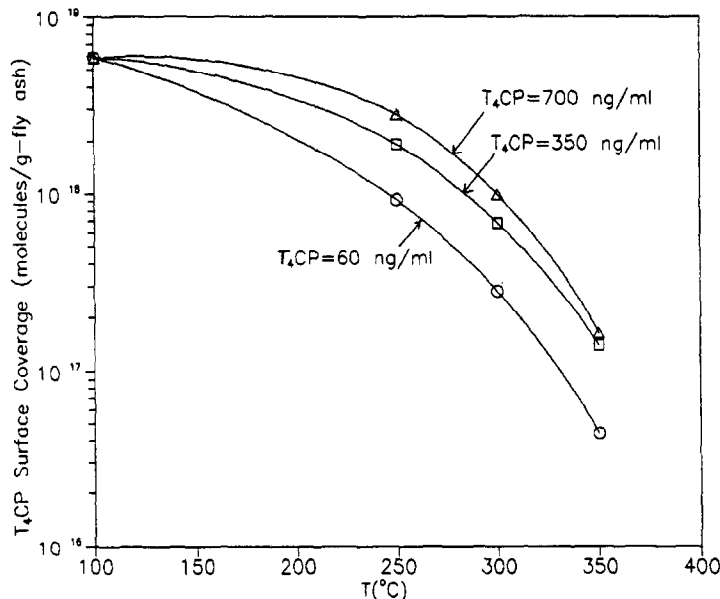


Fig. 3. Equilibrium surface coverage of  $T_4CP$  in helium as a function of gas-phase concentration and temperature, 0.1 g fly ash plus 0.9 g glass beads, He-flow 80 ml/min.

from the three different gas-phase concentrations, spanning more than an order of magnitude, converged. The calculated coverage is  $5.85 \pm 0.05 \times 10^{18}$  molecules/g fly ash (or sites/g fly ash), and seems to correspond to a fractional surface coverage of 1.0, i.e., all of the adsorption sites were covered. This value is in remarkable agreement with theoretical calculations, about  $2 \times 10^{18}$  sites/g fly ash, for a typical fly ash [32]. Assuming that  $N_m = 5.85 \times 10^{18}$  sites/g fly ash, the fractional surface coverage,  $\theta_s$ , over these ranges of concentrations and temperatures can be calculated.

Attempts to fit the adsorption data for chlorophenol in helium to a Langmuir adsorption isotherm were unsuccessful, which illustrates the highly heterogeneous nature of the fly ash surface. A variation of the Langmuir expression, known as the Freundlich isotherm, can be derived approximately by assuming an exponential distribution of adsorption site energies [35, 36], resulting in the expression

$$\theta_s = cP_g^n \quad (11)$$

where  $c$  is a constant and  $n$  is less than one.

For a plot of  $\ln \theta_s$  against  $\ln P_g$  for three temperatures (250°, 300°, and 350 °C), the slope at each temperature represents  $n$ , the exponent of the Freundlich isotherm. The calculated value for  $n = 0.50 \pm 0.05$  leads to

$$\theta_s = cP_g^{0.5 \pm 0.05} \quad (12)$$

with some uncertainty in the value of the exponent, due to the limited number of data points and  $c$  is some unknown function of temperature.

In the presence of oxygen, the surface coverage of chlorophenols was lower by factor of at least four even at 100 °C; as oxygen concentration increases, the apparent surface coverage of chlorophenols decreases, presumably due to irreversible reactions, since only a fraction of the phenol can be recovered by extraction.

Focusing on experiments for which chlorophenol conversions were relatively small (less than 30%), the fixed-bed reactor was modeled as a differential reactor. In these cases, the gas-phase concentrations, and presumably the surface coverages, varied about  $\pm 15\%$  throughout the bed, well within experimental and analytical errors intrinsic to these experiments. A qualitative judgement as to the relative merit of the Langmuir–Hinshelwood (LH) or Eley–Rideal (EL) mechanisms can then be made.

Introducing the adsorption isotherm for chlorophenols predicted by Eq. (12) into the Langmuir–Hinshelwood mechanism shown in Eq. (6) leads to

$$r_{LH} = k''_{LH} P_g \quad (13)$$

where  $k''_{LH}$  is a global rate constant incorporating the temperature-dependent proportionality constant from the Freundlich isotherm. Fig. 4 is a plot of the Langmuir–Hinshelwood rate coefficients vs.  $1/T$ . The  $r^2$  was calculated to be = 0.997 (vs. 0.978 for the Eley–Rideal model) and an activation energy,  $E_{a,LH} = 42$  kcal/mol. For  $T_4CP = 700$  ng/ml and at 350 °C, the rate of PCDD formation is about 20  $\mu\text{g/g}$  fly ash min. Although this experimental rate approaches incinerator rates, the laboratory gas-phase precursor concentration is more than three orders of magnitude greater than typical incinerator concentrations, which can be on the order of 0.1 ng/ml ( $100 \mu\text{g/m}^3$ ). If one applies the  $P_g$ -dependence to the first power (and  $100 \mu\text{g/m}^3$ ) to the

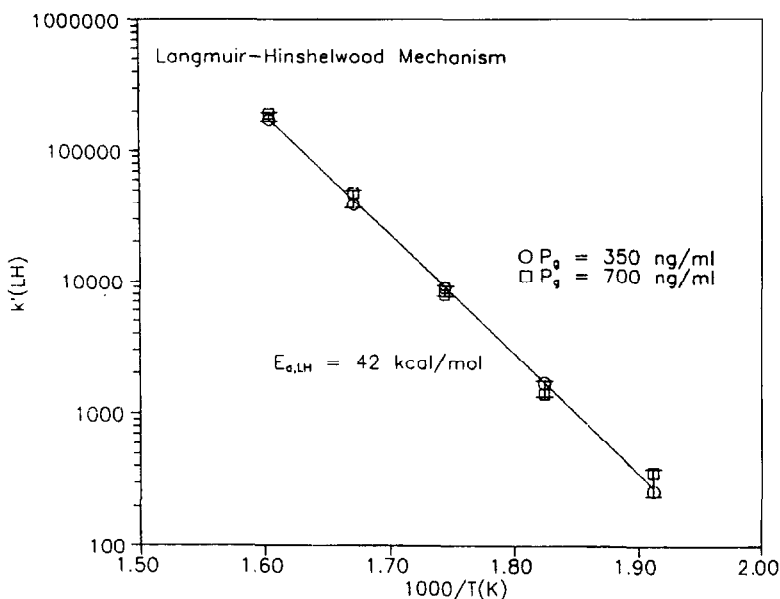


Fig. 4. Experimental Langmuir-Hinshelwood rate constants,  $k'_{LH}$ , for low conversion of T<sub>4</sub>CP on fly ash, T<sub>4</sub>CP = 350–700 ng/ml, T = 250–350 °C, 10% O<sub>2</sub> at 80 ml/min;  $r^2 = 0.997$ .

laboratory-based rate expression, the predicted incinerator PCDD-formation rate is about  $3 \times 10^{-4}$  µg/g fly ash min, i.e., of a magnitude comparable to de novo rates. This result is uncorrected for T<sub>4</sub>CP-recovery (about 75%). In the Freundlich isotherm, the  $n = 0.5$  dependence on gas-phase precursor concentration suggests that the energy distribution of sites on fly ash is highly nonideal and very high energy adsorption sites may be present. These highly energetic sites, or 'super-active' sites, postulated on the basis of a modeling analysis (cf. below, Section Modeling) might be responsible for the reaction rates observed in actual incinerators. A low gas-phase precursor concentration may be sufficient to cover such sites with reacting precursors.

In a recent study [37] of the reaction of phenol over fly ash in the presence of HCl and oxygen (to form mainly PCDD, above 327 °C) the reaction order in phenol was reported to be zero.

Chlorophenols are more reactive precursors than chlorobenzenes. Competition experiments between CPs and 1,2,4,5-tetrachlorobenzene lead to reactivity ratios, CP/T<sub>4</sub>CB = 16–52 [22, 23].

## 5. Pathways to PCDF

PCDF, particularly tetrachloro and pentachloro congeners, contribute substantially to the PCDD/F toxic equivalent; but the reactions of chlorophenols lead predominantly to PCDD with little or no PCDF, at these low temperatures.

Since the mechanism of the *de novo* reaction is not well understood and its apparent rate is not fast enough to explain PCDD/F-formation over short time scales, it is important to look for other sources of PCDF.

A review of the literature clearly establishes preferred laboratory routes to PCDF, albeit generally at temperatures higher than the 'de novo window'. In batch experiments in sealed quartz ampoules with trichlorobenzenes, tetrachlorobenzenes, and pentachlorobenzenes in the presence of air at 620 °C for 60 s PCDF-yields far exceeded PCDD-yields [38, 39]. From similar reactions using PCBs (550–850 °C, 60 s) PCDF only was reported. Beard et al. [40] showed that dibenzofuran was chlorinated by Cl<sub>2</sub> or HCl in the presence of ferric chloride at 220–540 °C. From the reaction of 1,1,1-trichloroethane and carbon tetrachloride (in hexane) PCDF-yields were about 100 × PCDD-yields (with peak yields occurring at 331 °C).

Temperatures much higher than 350 °C appear to be required to form PCDF from chlorophenols. So far it is not possible, however, to extract rate information from these types of studies (cf. Section 7).

## 6. Other C, H, O, Cl-combination

It is probably no exaggeration to state that under appropriate condition almost any combination of C, H, O, Cl in organic compounds (as well as inorganic compounds, i.e., chlorides) will form some PCDD/F. Inclusion of such compounds into the *de novo* designation would mean the broadest possible definition of that term.

Recent examples of PCDD/F-formation from simple gaseous precursors include propene/HCl/FA [41], pentane/HCl/sand [42], benzene/FeCl<sub>3</sub> [43] phenol/HCl [44], 2,3-dimethyl-1-butene/FA which yielded mostly tetra-hexa congeners with PCDD/PCDF < 1 and a maximum yield at 500 °C [45], anthraquinone derivatives/CuCl<sub>2</sub> [46], and results [40] cited above which show the diversity of possible precursors. Few, if any, of these experiments have, however, yielded kinetic information and since in most instances reactant concentrations far exceeded those that might be found in combustors, it is difficult to ascribe a precise role to such reactions in forming PCDD/F during incineration of different wastes.

The fact that MSWI-incinerator fly ash can be extracted exhaustively with organic solvent and the extracted fly ash heated to produce more CB, PCDD/F, etc. suggests that all elements needed can be furnished by the fly ash, i.e., fly ash is a reagent as well as a catalyst. Another interesting observation, for example, is the shift in congener distribution; with increasing temperatures the proportion of tetrachloro and pentachloro congeners increases, suggesting the presence of a hydrogen source in the fly ash in the *de novo* synthesis; and, as noted above, in the presence of oxygen the formation rates are much faster, but the incorporation of gaseous oxygen into the PCDD/F-structure has not been proven.

In experiments with a 'model' fly ash, it was demonstrated that C–Cl bonds could arise from KCl and CuCl<sub>2</sub> in the model mixture [9]. This seems to support a Deacon-type reaction which would yield Cl<sub>2</sub>.

There is much older literature on this topic, cf. Ref. [47], and the number of possible experiments and experimental designs is virtually endless [3]. Since relative amounts of chlorophenols and chlorobenzenes are so abundant in MSWI-flue gases,  $(CB + CP)/PCDD/F > 10^3$ , it would need to be shown that the rates of PCDD/F-formation from precursors other than CB and CP are at least comparable. In principle, synthesis from simple molecules is feasible (cf. also reaction schemes of the type shown in Ref. [48]).

## 7. Rapid formation/combustion intermediates

Measurements of PCDD/F at the exit of a secondary combustion chamber, at the inlet of an APCD (such as an ESP) and at its exit (stack), often have shown progressively increasing levels of these compounds, suggesting formation as the gases cool. In addition, evidence for phase shifts has been presented. Thus, PCDD/F at the inlet of an ESP tend to be predominantly in the particle phase, whereas at the exit gas-phase PCDD/F appear to dominate (based on front half/back half analysis of the MM5- or Method23-trains). As previous calculations have demonstrated [3], if 95% of all PCDD/F is on particles and 95% of such particles are removed the PCDD/F concentration between inlet and outlet should decrease by 90%, contrary to the increases that have been reported [28] which can be as high as a factor of 100 [49]. Since the PCDD/F particle loadings on inlet particles and collected particles are not drastically different, desorption from collected particles seems unlikely (it is also not favored by temperature). The question then is: can PCDD/F be formed during the gas-phase passage time through the APCD, either in the gas phase, on uncollected particles, or both. As pointed out above, this requires rates of  $10\text{--}10^3 \mu\text{g/g min}$ , rates not exhibited by the *de novo* reaction (as defined in Section 2).

Recent laboratory and pilot plant experiments have shown that PCDD/F can form rapidly at relatively low temperatures. Fängmark et al. [50, 51] reported on the combustion of pelletized synthetic RDF in a fluidized bed linked to a cooling section. When this cooling section was held at  $340^\circ\text{C}$  large quantities ( $>1000 \text{ ng/m}^3$ ) of PCDD/F were formed within 0.8–3 s; at higher ( $400\text{--}500^\circ\text{C}$ ) and lower ( $250^\circ\text{C}$ ) temperatures yields were much lower.

Gullett et al. [52] injected MSWI-fly ash downstream of a natural gas combustor and sampled 1–3 s further downstream; PCDD/F-quantities increased 2–100 fold over those originally present in the injected fly ash in the  $300\text{--}370^\circ\text{C}$  range. Exhaustive extraction of this fly ash prior to use to remove any PCDD/F present had virtually no effect on formation rates. Concentrations exceeded  $10\,000 \text{ ng/m}^3$  in some instances, with about 50% of PCDD/F associated with collectible particles.

We combusted 1,2-dichlorobenzene in heptane in a spouted bed combustor in the presence of sand or quartz and sampled in the bed, i.e., below (upstream of) the flame and at two locations downstream where there was either a rapid quench of the gas temperature ( $430\text{--}125^\circ\text{C}$ , profile q) or a near isothermal condition ( $430\text{--}380^\circ\text{C}$ , profile i). Because the temperature at the SC-location (Fig. 5) was the same in all experiments ( $430^\circ\text{C}$ ) and the equivalence ratio was constant (0.55), the data support

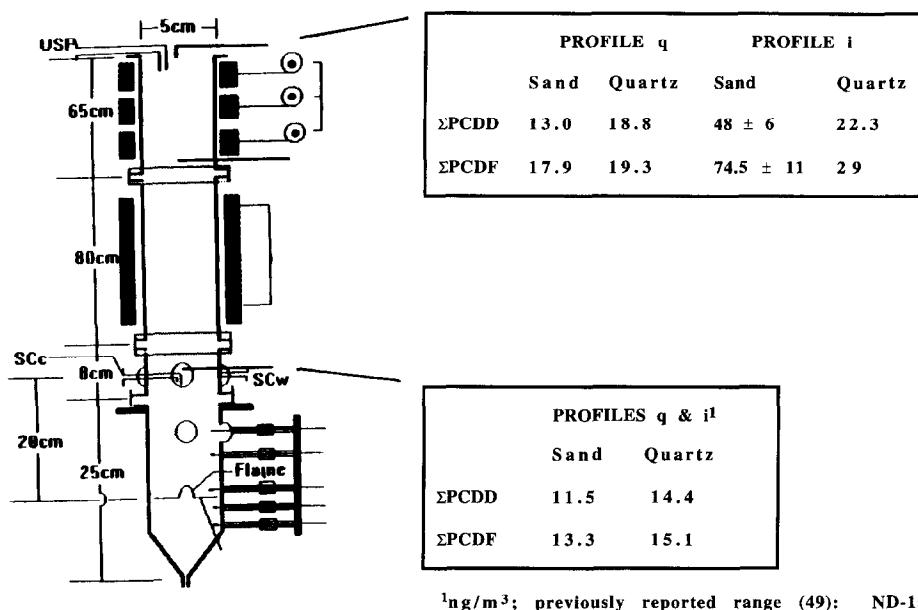


Fig. 5. PCDD/F-yields from the spouted bed combustion of 1,2-dichlorobenzene/heptane using either sand or quartz as bed material. Residence time between  $S_c$  and USP is  $\sim 4$  s, where  $S_c$  = sampling cross and USP = upper sampling port.

formation of PCDD/F in the cooler region for profile i, but not for profile q (quench). For profile q, sand and quartz gave similar concentrations; under profile i conditions, PCDD/F concentrations rose by about a factor of four when sand was present. Sand and quartz particles in the post combustion region arise from bed attrition; these particles are much ( $\sim 50\% < 5 \mu\text{m}$ ) smaller than the bed particles ( $\sim 1 \text{ mm}$ ). Quartz which is nearly pure  $\text{SiO}_2$  (99.995%) did not appear to promote PCDD/F-formation; the sand used is only 77.6%  $\text{SiO}_2$  and contains trace metal oxides such as Fe, Ca, Ti, and Mn. Also interesting is the finding that profile i gives PCDD/PCDF ratios  $< 1$  from a single precursor [53, 54], with  $\text{T}_4\text{CDF}$  as major product.

The apparent reactivity of fine attrited sand particles in the 430–380 °C temperature range suggest that model catalysts and fly ash may bring about both a higher formation rate and a lowering of the temperature. This work is in progress. Collectively, these results confirm that formation of PCDD/F may be rapid (rates  $> 10^2 \mu\text{g/g min}$  can be calculated from some of these results) and that formation can occur in a temperature window that corresponds most closely to the region between a secondary combustion chamber and an APCD in an actual incinerator. Though these three types of investigations involve very different fuels and combustors, the preferred formation of a PCDD/PCDF ratio  $< 1$  suggests a certain similarity in precursors leading to PCDD/F.

## 8. Fly ash properties

The concept of fly ash reactivity is one that should be exploited and, if possible, quantified, if further understanding of PCDD/F, and their precursors, formation is to be gained. Fly ash reactivity encompasses fly ash as a reagent (a source of C, H, O, Cl), i.e., *de novo* reactions and as a catalyst. What should be precise quantitative measures, however, of reactivity and how would these relate to the considerable body of knowledge on size distribution, chemical composition, and surface area?

Carbon gasification (to CO + CO<sub>2</sub>) is catalyzed by fly ash and it was shown that there are rate differences between fly ashes, with coal fly ash being inert. Are these differences due to the nature of the carbon or trace metals that could act as catalysts? Results shown in Table 1 clearly suggest that there may be a relationship between C-content of a fly ash, carbon gasification rate and PCDD/F- and CB-formation. Another interesting observation is an apparent relationship between inorganic chloride and organic chlorine cited above [14].

Several authors have demonstrated the catalytic effect of copper in laboratory experiments; however, the results are far from allowing a single conclusion as to the role of copper salts. For example, the highest yield of PCDD/F in carbon oxidation was obtained in the presence of 0.1% CuCl<sub>2</sub>; at higher CuCl<sub>2</sub>-concentrations yields decreased before increasing again (at 5% CuCl<sub>2</sub>); the range of the PCDD/F ratios in these experiments was cited above [20]. One should not overlook results from an incinerator campaign in Denmark [55] where the amount of copper was progressively increased, but the correlation between PCDD/F and copper appeared to be a negative one.

Fly ash surface areas are small when compared to heterogeneous catalysts [29, 30]; the heterogeneous nature of fly ash makes it unlikely that fly ash has anything resembling a uniform surface area or composition. The presence of carbonaceous material in pockets or patches that possess much higher surface area than the average may occur. In addition, shape and internal surface (though probably low) can vary between particle sizes. This is the only way in which results [29] such as higher surface area (36.93 m<sup>2</sup>/g) for larger particles (150–230 μm) can be explained (a smaller size range, 21–24 μm, had 7.78 m<sup>2</sup>/g). Trace metal composition, speciation and behavior on leaching have been reported [29, 30, 56–59]. There is no direct way at present to relate the physical/chemical measurement in a quantitative manner to fly ash reactivities as discussed above.

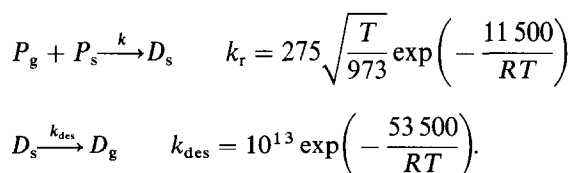
## 9. Modeling of PCDD/F-formation

Modeling the formation of PCDD/F in MSWIs is a formidable task; its difficulty is compounded not only by a lack of parameter control on incinerators, large differences between incinerators, and a paucity of measurements, but also by a lack of intrinsic kinetic information from laboratory experiments. Most of the modeling has addressed PCDD or PCDF because the number of isomers/congeners is so large, in spite of the fact that some reactions give very specific products, i.e., pentachlorophenol yielding

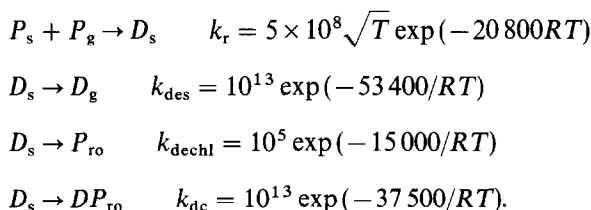
octachlorodibenzo-*p*-dioxin. Modeling will help to systematize diverse pieces of information but, most importantly, help focus on key parameters in future laboratory experiments and approaches to control.

Shaub and Tsang were the first to propose both a gas phase [60] and a surface [32] mechanism for PCDD/F-formation. Strictly speaking the gas-phase mechanism addressed formation of PCDD from CPs using an elementary reaction kinetics approach, where many individual reaction parameters were set so as to favor PCDD-formation. This approach could not reproduce observed incinerator quantities at APCD-temperatures. This mechanism with some ‘adjustments’ appears capable of predicting PCDD-levels at higher ( $\sim 500$ – $600$  °C) temperatures [61].

The two-step heterogeneous surface mechanism consisted of



The rate coefficients  $k$  and  $k_{des}$  were later modified by Wiesenbahn et al. [62] to obtain a fit to the Vogg and Stieglitz de novo data [5]. These models gave a poor fit to the Dickson data [24–26]. We developed a four-step model which gave an excellent fit to Dickson’s data (cf. Ref. [28], Fig. 5). The model consists of reaction, desorption, dechlorination, and decomposition with assumed pre-exponentials and activation energies:



It is reasonable to include dechlorination and decomposition into the model: at temperatures above 300 °C the congener distribution shifts progressively towards lower chlorinated species; at the same time the total yield of PCDD decreases.

Without further parameter adjustments but introducing a temperature dependence for the surface coverage of fly ash as well as a fly ash size distribution, this model compared favorably with measurements taken at two incinerators between the secondary combustion chamber exit and the APCD-inlet, a region where net formation can occur also [63]. It was shown further that the model results were very sensitive to assumptions about the magnitude of the activation energy of desorption. Further details on this model, an analysis of pertinent time scales, have been published [64].

A model formulation of this type assumes that all sites on a fly ash particle show the same behavior leading to PCDD-formation. Given the heterogeneous nature of fly ash a distribution with site activities seems more likely. Indeed, incinerator fly ash is



a highly complex heterogeneous mixture of metals, their oxides, chlorides, sulfates, etc., and nonmetals. Recent adsorption studies [22] have suggested that a fly ash surface consists of a distribution of site activities with respect to adsorption of 2,3,4,6-tetrachlorophenol. Such sites may exhibit different kinetics and, hence the total PCDD/F concentration at any time would include contributions from all types of sites. For the sake of simplicity, a new model which lumps the distribution of catalytic site activities in two categories is proposed: superactive and active catalytic sites, i.e., the distribution of kinetic time scales is reduced to two ranges, termed (a) short (or fast PCDD/F-formation) time scale ( $\sim O(1-10\text{ s})$ ), and (b) long (or slow PCDD/F-formation ( $\sim O(10^2-10^3\text{ s})$ )).

The short time scale, characterizes the initial rate of PCDD/F formation. It is hypothesized to be associated with the presence of superactive sites (with respect to PCDD/F formation) on the fly ash surface which act early in the process while the long time scale formation is hypothesized to be due to active (lower reactivity) sites. Hence, the distinct character of this model lies in the hypothesis of two types of sites (in a global sense) instead of one, as previous models.

A qualitative outline of this model follows. The fly ash formation process takes place mainly in the primary and secondary combustion chambers and the boiler where particles generated in the combustion chamber can be enriched via condensation of volatile metal vapors. Such 'fresh' fly ash particles may possess these highly active sites, and thus provide a rationale for the hypothesis of superactive sites. The bigger particles collect in the ducting and boiler regions while the small particles move with the flue gases. Consequently, there are two kinds of particles in particle collection equipment: collected and uncollected particles. The collected particles may spend about  $O(1000\text{ s})$  there, while uncollected particles may have a residence time  $O(1\text{ s})$  only. A major portion of the particle-bound PCDD/F is collected in the particle collection equipment whereas all desorbed PCDD/F and as well as PCDD/F associated with uncollected (as well as reentrained) particles enters the stack. These particles adsorb precursor molecules by either physisorption or chemisorption during their passage through the incinerator. Gas phase precursor molecules constantly impinge upon these adsorbed molecules with subsequent formation of PCDD/F.

The rapid formation of PCDD/F would occur on superactive sites. Based upon the short time scale laboratory and pilot plant experiments (cf. Section 7) there is a time  $O(1\text{ s})$  during which PCDD/F form rapidly at a rate of  $10-10^3\text{ }\mu\text{g/g fly ash min}$ , depending upon the operating conditions. The characteristic time scale is given by  $1/k_{r,sa}$  where  $k_{r,sa}$  is the formation rate constant for superactive sites. An order of magnitude estimate of the PCDD/F formation rate in this regime can be made. In an incinerator, the PCDD/F concentration measured at the exit of the APCD may include contributions from both the particle and gas phase. Hence

$$D_{\text{total}} = N_{\text{p,out}} \times D_{\text{s}} + D_{\text{g}}$$

where  $N_{\text{p,out}}$  is the exit concentration of particles ( $\text{g/m}^3$ ). Consider a specific case of  $D_{\text{total}} \sim 50\text{ ng/m}^3$  and  $N_{\text{p,out}} \sim 0.05\text{ g/m}^3$ . Assuming no desorption ( $D_{\text{g}} \rightarrow 0$ ), this gives

the upper limit for  $D_s$ ), and no separate gas-phase contribution;

$$D_s = \frac{D_{\text{total}}}{N_{\text{p,out}}} \sim \frac{50 \text{ ng/m}^3}{0.05 \text{ g/m}^3} = 1000 \text{ ng/g fly ash (1 } \mu\text{g/g)}$$

$$r_{\text{formation}} = \frac{D_s}{\Delta t} = \frac{O(1 \mu\text{g/g})}{O(1\text{s or } 1/60 \text{ min})} = 60 \mu\text{g/g fly ash min}$$

where  $r_{\text{formation}}$  (maximum rate in Ref. [3, Table 5]) is the calculated rate of PCDD/F-formation. Similar results can be obtained from the laboratory and pilot plant scale experiments cited. Superactive sites are postulated to be limited in number and are a function of the past time/temperature history of the fly ash. Their number would decrease as a result of PCDD/F-formation, unless desorption occurred.

Rapidly accumulated PCDD/F can be destroyed and this perhaps could occur on super active sites. Experimental data reported by Ross et al. [65] clearly indicates that the PCDD/F concentration decreases to a steady value from a large initial value when reaction times of  $O(100 \text{ s})$  are used. So a model should account for the rapid destruction of PCDD/F accumulated. When there is little PCDD/F desorption (high activation energy) destruction may occur; however, if the particles on which PCDD/F have been formed leave the characteristic temperature region rapidly, the reaction may be quenched and PCDD/F-concentrations on particles could be high.

Under laboratory conditions (long time scales) in fixed beds of fly ash PCDD/F form at considerably slower global rates, as was noted earlier. The most salient feature of the long time scale data is an established ‘bell’-shaped curve of  $D_s$  vs. temperature with a maximum in  $D_s$  in the temperature window of 250–350 °C (Fig. 1); there is a second temperature peak at about 450 °C indicating another ‘temperature window’ [11].

Writing a mass balance for superactive sites

$$\begin{aligned} & \text{total number of superactive sites present } (S_{\text{sa}}) \\ & = \text{number of super active sites occupied by precursor molecules} \\ & \quad + \text{number of superactive sites occupied by PCDD/F} \end{aligned}$$

or

$$\theta_{\text{s,sa}}(t = 0) = \theta_{\text{s,sa}}(t) + \theta_{D_s, \text{sa}} = \text{constant}; \quad (14)$$

where  $\theta$  is the surface coverage. Note that  $\theta_{\text{s,sa}}(t = 0)$  is constant, determined by prior fly ash history and adsorption equilibrium relationships, while  $\theta_{\text{s,sa}}(t)$  and  $\theta_{D_s, \text{sa}}$  vary with time. These two time-dependent surface coverages are related to each other by the PCDD/F-formation kinetics:

in the ER formulation:

$$\frac{d\theta_{\text{s,sa}}(t)}{dt} = - \frac{d\theta_{D_s, \text{sa}}(t)}{dt} = - k_{\text{sa}} P_g \theta_{\text{s,sa}} \quad (15)$$

(or  $-k_{sa}\theta_{s,sa}^2$  in the LH-formulation). It can be shown that

$$\theta_{s,sa} = \theta_{s,sa,0} \exp\left(-k_{r,sa}\left(\frac{I}{n_s}\right)t\right) \quad (16)$$

where  $I = \text{impingement rate} = P_g/\sqrt{2\pi MkT}$ ,  $n_s = \text{total number of sites per area}$ , and  $k_{r,sa}$  is the first order formation rate constant. This expression gives the rate at which the precursor is depleted on the sites due to PCDD/F-formation reaction.

In a similar way active sites, the second type of sites, are characterized. However, active sites are hypothesized to be in large excess with respect to PCDD/F-formation; consumption of sites by product molecules or subsequent reactions does not change the formation rate (the reason for this postulate is the lack of desorption of PCDD/F under original de novo conditions). In this case, the site material balance is simply

$$\theta_{s,a}(t) = \theta_{s,a,0}. \quad (17)$$

Since  $\theta_{s,a}(t)$  is assumed to be a constant, the surface coverage is simply denoted as  $\theta_{s,a}$ . Eqs. (16) and (17) give the time dependence of the effective surface coverage. On active sites it is a constant, but it decreases exponentially on superactive sites. The surface coverages,  $\theta_{s,sa}$  and  $\theta_{s,a}$ , are related to the apparent surface coverage  $\theta_s$  (what one would measure if the fly ash were extracted and analyzed for precursors) by the simple relationship,

$$\theta_s = \frac{S_{sa}}{n_s}\theta_{s,sa} + \frac{S_a}{n_s}\theta_{s,a}. \quad (18)$$

Combining the surface coverage histories with the specific kinetics of the sites, PCDD/F surface and gas-phase concentrations can be obtained. As described earlier, the global chemical processes taking place on these sites are the same as those described in previous models – surface reaction, desorption, surface destruction and dechlorination.

For active sites the resulting steady state  $D_s$  (particle-associated PCDD/F, molecules/g fly ash) can be formulated as

$$D_{s,a} = k_{r,a}\left(\frac{I}{n_s}\right)\frac{\theta_{s,a}S_a\Omega}{\beta_a} \quad (19)$$

where

$$\beta_a = k_{des,a} + k_{dechl,a} + k_{dec,a}$$

$$S = \text{number of sites per m}^2$$

$$\Omega = \text{fly ash surface area, m}^2/\text{g}$$

The exponential dependence for superactive sites (Eq. (16)) means that as  $t$  increases the exponential becomes small. This is in accord with the model hypothesis that destruction takes over on superactive sites after rapid formation peaks. Consequently, over long times the PCDD/F-contribution from superactive sites to the total could be small.

A result from the model calculation is shown in Fig. 6 for four different values of the  $S_{sa}/n_s$  ratio;  $D_s$  is proportional to this ratio. The right-hand side of the curve represents PCDD/F-formation on active sites over long times. These calculations were carried out by assuming or deriving values for the rate constants from the studies described earlier, and  $P_g = 7.5 \times 10^{10}$  molecules/cm<sup>3</sup> ( $\sim 25$   $\mu\text{g}/\text{m}^3$ ) and  $I = 2.34 \times 10^{18}$  collisions/m<sup>2</sup>s at 250 °C. This results in an initial formation rate of 83  $\mu\text{g}/\text{g}$  min, i.e., of similar order of magnitude as calculated from the rapid formation type experiments and incinerator data.

Two groups have used statistical approaches to gain insights into factors controlling PCDD/F-formation. Gullett et al. [52] considered O<sub>2</sub>, HCl, Cl<sub>2</sub>, temperature, residence time, and quench rate. They treated the data from 22 pilot plant runs by stepwise regression analysis to identify the most important predictors; oxygen concentration,  $T_{\text{duct}} (\leq 376$  °C) residence time ( $t < 4.6$  s), and quench rate strongly influenced

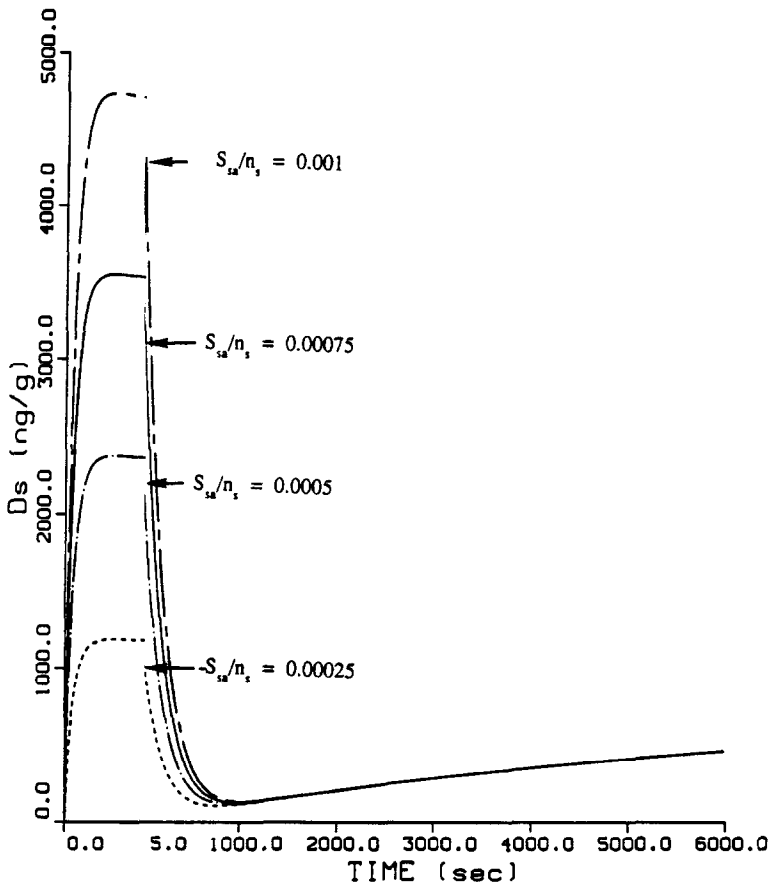


Fig. 6.  $D_s$  (= PCDD on particles) yield as a function of time and  $S_{sa}/n_s$  at 250 °C and  $P_g = 7.5 \times 10^{10}$  molecules/cm<sup>3</sup>; note scale change between 5.0 and 1000.0 s.

PCDD/F-rate and yield (this work is described in more detail elsewhere in this issue). Fängmark et al. [50, 51] used a full factorial design in their experimental program and analyzed their results via principal component analysis. A statistical correlation between PCDD/F and chlorinated aromatic compounds has been reported [66].

At this time, PCDD/F-modeling is in its infancy, partly because the data base is so meager. Consequently, no particular approach should be excluded a priori.

## 10. Discussion

What are the implications of current laboratory research for the operation of incinerators?

An operating municipal solid waste incinerator might be thought of having two reaction regimes for PCDD/F formation: a particle-rich regime, describing fly ash particles deposited in different regions of the incinerator such as the ducting walls, ESP collection plates, and fabric filters which are ultimately collected in hoppers for future disposal (particle concentrations are similar to undiluted fly ash in a fixed-bed reactor and a residence time on the order of minutes to hours) and a second regime, the particle-lean phase, describes the free gas stream in an incinerator where the (uncollected) particle concentration is very low, on the order of 0.05–5.0 g/m<sup>3</sup>, and the residence time is on the order of seconds before exiting through the stack. In a fixed-bed reactor this latter condition can only be approached by diluting the fly ash with inactive glass beads and by assuming no significant mass transfer limitations [67].

The particle-rich phase, where the fly ash is essentially in a packed-bed configuration in the incinerator, is the easiest to investigate and simulate experimentally. PCDD/F concentrations on collected fly ash from MSWIs typically range from 10 to 1000 ng/g fly ash. Reported de novo synthesis rates from the MSWI fly ash studies range from 10<sup>-4</sup> to 10<sup>-1</sup> µg/g fly ash min at optimum temperatures around 300 °C. Assuming an average residence time for collected particles equal to 30 min results in PCDD/F yields ranging in 30–3000 ng/g fly ash for these fly ashes, in excellent agreement with measured amounts from actual incinerators. One might conclude, therefore, that de novo synthesis by itself can explain PCDD/F concentrations on collected particles from incinerators.

However, one needs to consider contributions from gas-phase precursors present in the flue gas stream, such as chlorophenols, reacting on collected fly ash. In an actual incinerator, a chlorophenol may only react on the surface layer of collected particles. The subsequent PCDD/F formation rate, although potentially high in this thin reaction zone, may be quite small on a *per gram* fly ash basis, since the bulk of the gas-phase precursor could not penetrate the fly ash layer before being converted. For example, when 40 ng/ml of T<sub>4</sub>CP was flowed through 1.0 g of undiluted fly ash, the relative contributions of de novo synthesis of PCDD/F and PCDD formed from the gas-phase precursor was about 1:1. However,  $P_g = 40$  ng/ml is about 500 times greater than reported total chlorophenol incinerator concentrations. Extrapolating to incinerator conditions using the global rate expression derived for PCDD-formation from T<sub>4</sub>CP (Eq. (13)) results in PCDD formation from the chlorophenol 100 times

slower than the laboratory result. The new ratio of PCDD formation from de novo synthesis to gas-phase precursors as applied to incinerator conditions is then about 100:1.

The free-gas stream in the ESP-part of the incinerator, where the particle concentration is very low, is termed the particle lean phase. The concentration from de novo synthesis of PCDD/F in this case is expected to be very small due to the low particle concentration. For the range of de novo synthesis rates near 300 °C, an uncollected particle loading in an ESP of 0.1 g/m<sup>3</sup> and a residence time of one second, the resultant contribution from de novo synthesis of PCDD/F would range in 0.002–0.2 ng/m<sup>3</sup>, i.e., orders of magnitude lower than most MSWI stack data.

If a typical gas-phase chlorophenol concentration is 100 µg/m<sup>3</sup> (of molecular weight of 200), the gas-phase precursor concentration would be estimated as  $P_g = 3 \times 10^{11}$  molecules/cm<sup>3</sup>. From adsorption experiments the fractional surface coverage ( $\theta_s$ ) of chlorophenols predicted from the Freundlich isotherm is about  $2 \times 10^{-4}$ , corresponding to  $10^{15}$  sites/g fly ash (or 400 ng/g fly ash). Assuming a particle loading of 0.1 g/m<sup>3</sup> results in a surface bound chlorophenol concentration of  $10^8$  molecules/cm<sup>3</sup> of flue gas. In other words, the ratio of gas-phase chlorophenols to solid-phase chlorophenol is on the order of  $10^3$ , i.e., the number of gas-phase chlorophenol molecules available per active site is very high. Assuming no mass transfer limitations and fast adsorption rates, breakthrough conditions such as studied experimentally might be achieved. Under these conditions, laboratory PCDD formation rates approach those in incinerators. Additionally, the majority of PCDD formed from these reactions would desorb into the gas phase, agreeing with sampling data from operating MSWIs.

One may speculate that in the free gas stream of an incinerator where the particle number density is small and the precursor to particle ratio is high, PCDD-formation reactions involving gas-phase precursors is the dominate mechanism.

The major shortcoming of this analysis is that it cannot explain frequently observed PCDD/PCDF-ratio <1. Although laboratory evidence exists (Section 5) that PCDF can be formed at higher temperatures, it seems unlikely that most of the PCDF would be formed there, since PCDD/PCDF ratios do not change significantly between the secondary combustion chamber exit and the stack. Homogeneous gas-phase condensation-type reactions could explain both PCDD and PCDF at higher (>500 °C) temperatures but not increases in concentration across ACPDs. At high temperatures (~650 °C) phenol can form dibenzodioxin and dibenzofuran which may subsequently be chlorinated, with Cl<sub>2</sub> being a much better chlorinating agent at lower temperatures than HCl [68], reactions that are also positively influenced by copper. There is a need for detailed studies of the role of Cl<sub>2</sub> and inorganic chloride salts in both the de novo and gas-phase precursor reactions on fly ash.

In a paper of this length it is not possible to discuss congener distributions in any detail. Yet these are of foremost importance, as much of the TEF (toxic equivalent factor) is found in the contributions from T4CDD and T4CDF and P5CDF. Earlier comments [69] continue to be applicable, namely that a laboratory experimental result may be considered relevant when the PCDD/PCDF-ratio, the congener group ratios, and the within – congener (isomer) patterns resemble those observed in incinerators.

Recent calculations [70] suggest that the electric field in an ESP could play an important role in determining PCDD/F-levels by facilitating OH-radical production at modest temperatures, thus increasing gas-phase PCDD (and perhaps PCDF) formation potential. Such calculations are supported by several observations, such as the (PCDD/F-concentrations with and without a corona discharge [71].

Both segmented and system approaches continue to be valid to generate new laboratory data. Their objective should be global (as well as detailed) chemical reaction kinetics of heterogeneous reactions together with detailed product analysis.

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