

## Formation of Polychlorinated Dibenzo-p-dioxins/Dibenzofurans in Waste Combustion: Role of Chlorine - Review

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### 1. Introduction

Many laboratory studies on formation of polychlorinated dibenzo-p-dioxins/dibenzofurans have assigned catalytic activity to fly ash.<sup>1,2</sup> Transition metal ions present in the fly ash appear to be responsible for this catalysis, especially Cu and Fe.<sup>3,4</sup> Carbon naturally present on fly ash, but also molecules adsorbed onto the fly ash like propene, serve as organic material for building PCDD/F.<sup>5,6</sup> It has been shown that the oxygen incorporated into PCDD/F formed from carbon, stems at least partially from the gas phase.<sup>7</sup>

Chlorine is present on fly ash in various forms. Fly ash investigated by Milligan contained up to 8% of inorganic Cl.<sup>5</sup> On the other hand, Stieglitz et al. showed the existence of C-Cl bonds in the carbon matrix on fly ash; the fly ash investigated contained 500-900  $\mu\text{g/g}$  of organic Cl.<sup>8</sup> Gas phase compounds, e.g. HCl, have been used as a chlorinating agent too.<sup>9</sup> In this paper, the role of Cl in PCDD/F formation is examined.

### 2. Inorganic Chlorine

#### a) Solid phase

Blaha reports on experiments with a model fly ash of  $\text{SiO}_2$ , activated carbon, metallic Cu and 1.1% or 6.6% KCl at 300 °C. In this system, PCDD/F are produced, indicating that KCl acts as a source of Cl. With 6.6% KCl, 3.5 times more PCDD/F was formed than with 1.1%, suggesting that under these conditions Cl was a limiting factor.<sup>10</sup> In contrast, NaCl has little effect on PCDD/F formation from carbon at 300 and 600 °C.<sup>11,12</sup> No catalytic activity has been attributed to KCl or NaCl in PCDD/F formation, and therefore the presence of some catalyst (e.g. Cu) is required. The Cl could then be transferred from KCl or NaCl to form e.g.  $\text{CuCl}_2$ . At higher temperatures conversion to HCl is another possible pathway. NaCl is converted to HCl at 800 °C and appears to act as a chlorine source in the formation of chlorophenols from cellulose.<sup>13</sup> Chlorophenols are known precursors for PCDD.<sup>2</sup> Hence, NaCl could be a Cl donor at elevated temperatures, i.e. in the combustion chamber.

$\text{FeCl}_3$  is both catalyst and chlorine source for the chlorination of polycyclic aromatic hydrocarbons on fly ash. This reaction takes place through a direct Cl transfer from the metal chloride to the carbon atoms, following an electrophilic mechanism.<sup>4</sup> For chlorination reactions with  $\text{CuCl}_2$ , at least three different routes could be available. Schwarz has proposed

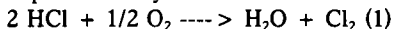
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for PCDD/F formation from carbon that chlorination by  $\text{CuCl}_2$  proceeds via a direct Cl transfer, as with  $\text{FeCl}_3$ .<sup>14</sup> Bruce et al. found that  $\text{CuCl}_2$  decomposes and forms  $\text{Cl}_2$  when heated under oxygen at 300 °C.<sup>15</sup> Finally, it could be involved in the Deacon reaction (see below).

## *b) Gas Phase*

HCl can provide the Cl necessary for PCDD/F formation from both small organic molecules, e.g. propene at 576 °C,<sup>6</sup> and carbon at 298-398 °C.<sup>9</sup> Both these studies were carried out on fly ash. At 700 °C, homogeneous gas phase chlorination of phenol with HCl yields o-chlorophenol.<sup>13</sup>  $\text{Cl}_2$  was used in the PCDD formation from phenol with various Cu catalysts.<sup>15</sup> Increasing the amount of  $\text{Cl}_2$  resulted in formation of more PCDD.

Griffin has advanced the Deacon reaction (1) to explain the role of HCl in chlorination reactions on fly ash.<sup>16</sup> Cu compounds in fly ash could act as Deacon catalysts.



In this theory, the HCl is converted to  $\text{Cl}_2$ , which then acts as the chlorinating agent on fly ash. Gullett et al. found that up to 1.3% of HCl reacts to form  $\text{Cl}_2$  over fly ash.<sup>17</sup> However, a number of observations made by various authors argue against the importance of the Deacon reaction on the fly ash surface. A run with a certain HCl flow, passed over fly ash, can be expected to contain ca. 100 times less  $\text{Cl}_2$  than a run with the same  $\text{Cl}_2$  flow, since the conversion of HCl is only ca. 1%. Still, HCl and  $\text{Cl}_2$  appeared to be equally efficient Cl donors in the PCDD/F formation from carbon on fly ash at 300-400 °C.<sup>9</sup> The Deacon reaction requires the presence of  $\text{O}_2$ , whereas 1,2,3,4,7,8- $\text{H}_6\text{CDD}$  can be chlorinated on fly ash with HCl in a  $\text{N}_2$  atmosphere.<sup>18</sup> Furthermore, in the fly ash catalyzed oxychlorination of ethylene, 30-60 times more chlorinated product was found than can be accounted for by the Deacon reaction.<sup>3</sup> Together, these observations suggest that the Deacon reaction might take place on the fly ash surface, but is certainly not a predominant pathway in chlorination by HCl.

## 3. Organic Chlorine

Dichloromethane and 1,2-dichloroethane act as Cl donor in PCDD/F formation from carbon at 300 °C on several model fly ashes,<sup>10</sup> and trichloroethylene chlorinates PCDD/F formed from toluene on fly ash at 425 °C.<sup>19</sup> These compounds are examples of small organochlorine compounds that participate in chlorination reactions on the fly ash surface. Other compounds are incorporated into the PCDD/F formed and act both as carbon and Cl source. Examples are chlorobenzenes<sup>20,21</sup> and chlorophenols<sup>2</sup>. Degradation reactions of PCDD/F produce lower chlorinated congeners,<sup>22</sup> and the Cl that is released in this pathway could be consumed in the chlorination of new PCDD/F.

PVC has been advanced as a possible macromolecular Cl source for PCDD/F formation, but its role is highly debated. It does produce PCDD/F in laboratory experiments when combusted in a fluidized bed at 300 °C (both in  $\text{N}_2$  and  $\text{N}_2/\text{O}_2$  mixtures).<sup>23</sup> As described above, the native carbon on fly ash contains C-Cl bonds,<sup>8</sup> and this Cl is incorporated into the PCDD/F molecules that are released in the oxidative breakdown of the carbon.

## 4. Comparison of Pathways

A comparison of the various chlorination pathways can provide some insight into the relative importance of each Cl source, both in laboratory experiments and in real incinerators. It is obvious that many transitions between inorganic and organic Cl occur. If Cl is transferred

from, e.g. NaCl, to carbon with  $\text{CuCl}_2$  as intermediate, the Cl is inorganic originally, but becomes organic prior to incorporation in PCDD/F.

The results summarized above show that at typical post combustion zone temperatures (200-500 °C) inorganic salts, HCl and  $\text{Cl}_2$ , small organochlorine compounds, PVC and pre-chlorinated (native) carbon can all participate in chlorination reactions leading to PCDD/F. Two important questions arise: i) Which of these sources is the most important?; ii) Is there a correlation between [Cl] and PCDD/F formation?

Question i) was investigated by Wikström et al. These authors compared the influence of  $\text{CaCl}_2$  vs. PVC on PCDD/F formation in a fluidized bed combustor burning synthetic waste at 880 °C. They found no significant difference in chlorinating capability.<sup>24</sup> Similar conclusions were reached by Lenoir et al., who found no difference between NaCl and PVC in PCDD/F formation from a refuse-derived fuel (RDF).<sup>25</sup> Halonen et al. reported that NaCl or tetrachloroethylene had no effect on PCDD/F formation in the combustion of aliphatic  $\text{C}_{10}$ - $\text{C}_{13}$  compounds in a liquid fuel burner.<sup>26</sup> These results suggest that the character of the Cl is not important. This could be explained by assuming that both solid inorganic and organic Cl are converted into HCl in the combustion chamber, i.e. with both types of Cl the actual chlorinating agent is identical. However, experiments burning synthetic municipal waste at 850 °C resulted in [HCl]:[solid inorganic Cl in fly ash] ratios of 5:1,<sup>13</sup> and significant amounts of inorganic solid phase Cl could be available in the post combustion zone for chlorination reactions.

Question ii) has been studied both in the laboratory and in the field. A dependence of PCDD/F formation on [KCl] or [ $\text{Cl}_2$ ] has been reported for formation on a laboratory scale from carbon and phenol respectively.<sup>10,15</sup> In both cases, the amount of Cl present was several orders of magnitude higher than the amount of PCDD formed and a zero-order dependence might have been expected. On the other hand, an investigation of industrial incinerators showed no correlation between PCDD/F formation and the amount of Cl in the feed.<sup>27</sup>

## 5. Conclusions

Laboratory studies dealing with the role of Cl in PCDD/F formation have shown that various potential Cl sources exist. Salts without catalytic activity (KCl, NaCl), catalytic metal chlorides ( $\text{CuCl}_2$ ,  $\text{FeCl}_3$ ), inorganic gases (HCl,  $\text{Cl}_2$ ), small organochlorine compounds (dichloromethane, chlorobenzenes, chlorophenols), PVC and carbon containing C-Cl bonds, can all provide Cl necessary for PCDD/F formation. The majority of this research was carried out in fixed beds, some of it in fluidized/spouted beds. Comparative studies of inorganic and organic Cl were carried out with the latter type, thus measuring 'in-flight' formation of PCDD/F. Using both types of approach, i.e. formation on packed beds and 'in-flight', is very useful, since both types of formation are likely to take place in real incinerators.

If the existing C-Cl bonds in the waste are nearly all destroyed in the furnace, no influence of the pre-existence of C-Cl bonds on PCDD/F formation would be expected. This appears to be the case, since inorganic and organic Cl seem to be equally good chlorinating agents. HCl would be an obvious intermediate from both solid inorganic and organic Cl sources. Further research is required to compare rates of chlorination by solid inorganic and organic Cl with chlorination by HCl. This can elucidate to what extent pathways not including HCl (e.g.  $\text{NaCl} \rightarrow \text{CuCl}_2 \rightarrow \text{C-Cl} \rightarrow \text{PCDD/F}$ ) play a role and at what temperature.

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Opposing results have been published regarding the influence of the total amount of Cl on PCDD/F formation: some authors did find a correlation, whereas others did not. Further research into this question is required, since this will help to assess the validity of fractioning/separating waste prior to incineration.

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