

### The Determination of the Role of Gaseous Oxygen in PCDD/F Formation on Fly Ashes by the Use of Oxygen-18

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#### 1 Introduction

The formation of PCDD/F on fly ashes in MSWI is mainly understood as a combination of heterogeneous oxidation and chlorination reactions<sup>1,2</sup>. The investigation of the oxidation reaction with labeled  $^{18}\text{O}_2$  in the gas phase has once been carried out by Olie and Schonenboom<sup>3</sup>, who used fly ash doped with activated carbon and copper-(II)-chloride. The conclusions drawn from this experiment can partly be ascribed to these compounds added to the fly ash.

Therefore, a series of experiments with untreated fly ashes of different origin has been carried out in a helium  $^{18}\text{O}_2$ -atmosphere in order to understand more about the oxidation process and the oxygen incorporation into the carbon matrix. The  $^{18}\text{O}$ -content found in the reaction products is of gas phase origin, while the  $^{16}\text{O}$ -content is mainly due to chemically bonded oxygen of the residual carbon of the fly ashes.

#### 2 Experimental

Three different fly ashes were heated at 350 °C in a constant flow of 30 ml per minute and a gas feed composition of helium with 5 % of oxygen with an 18-oxygen content of 91 %. The gas phase composition after reaction was measured online by mass spectroscopy (Leybold quadrupole-MS, mass range: 1-100 amu), using SIM-mode for the following gaseous compounds: He,  $\text{C}^{18}\text{O}$ ,  $\text{C}^{16}\text{O}$ ,  $\text{C}^{18}\text{O}_2$ ,  $\text{C}^{18}\text{O}^{16}\text{O}$ ,  $\text{C}^{16}\text{O}_2$ ,  $^{18}\text{O}_2$ ,  $^{16}\text{O}^{18}\text{O}$  and  $^{16}\text{O}_2$ .

Isotopic ratios of oxygen in chlorinated organics have been calculated from GC-MS-chromatograms of selected ions.

#### 3 Results and Discussions

##### Online Reaction Monitoring

The gas phase composition as a function of reaction time is shown in figure 1. The composition changes rapidly when reaction temperature is reached. The quick release of  $\text{C}^{16}\text{O}_2$  leads to an early concentration maximum after 8 minutes. The maximum values for  $\text{C}^{16}\text{O}^{18}\text{O}$  and  $\text{C}^{18}\text{O}_2$  are in the range of 12 and 18 minutes after the reaction was started.

Formerly physically and chemically bonded oxygen-16 on the surface of the residual carbon dominates in the oxidation products in the first period of the reaction. It is gradually being replaced by oxygen-18 of gas phase origin, which becomes predominant after 20 minutes.

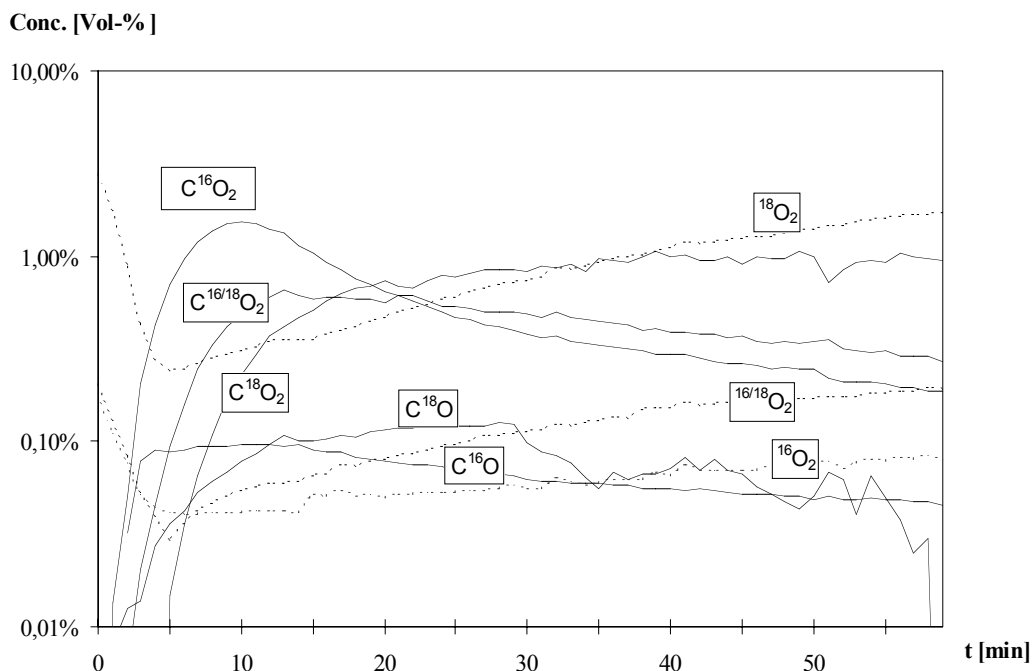


Figure 1 Online-mass-spectroscopy: concentrations of gaseous compounds vs reaction time

The oxygen-16 content in the oxidation products CO and CO<sub>2</sub> (39 to 54 %) still remains much higher than in the gas feed (~ 9 %). This surplus is due to the oxygen content of the residual carbon. More than 30 % of the oxygen emitted during the reactions is of solid phase origin.

#### Quantification of the <sup>16</sup>O-Enrichment in Organic Compounds by GC-MS

The ratios between <sup>16</sup>O and <sup>18</sup>O in chlorinated organics were calculated from GC-MS-chromatograms.

The content of <sup>18</sup>O in PCDD/ PCDF and chlorinated phenols is presented in table 1. Division of the values by the <sup>18</sup>O-content in the gas feed leads to the exact incorporation-rate of gaseous oxygen.

In summary: PCDD, PCDF and chlorinated phenols show a similar response towards oxygen incorporation from the gas phase, while the total isotopic content depends on fly ash type and aromatic body.

- (i) Higher chlorinated products contain lower amounts of <sup>16</sup>O and vice versa.
- (ii) Variations in isotopic ratios within the homologues in each experiment are very small.
- (iii) PCDD contain higher amounts of <sup>18</sup>O from the gas phase than PCDF

These results can be interpreted as follows:

(i) Higher chlorinated molecules may be formed from volatile precursors that move to the most reactive catalyst sites of the fly ash matrix, where chlorination and re-oxidation of the catalyst by gaseous oxygen occurs. The catalyst may also be responsible for oxygen transfer of formerly gaseous oxygen towards hydrocarbons.

Less volatile or bonded precursor structures of the carbon matrix containing carbon-bonded <sup>16</sup>O are likely to be the source of lower-chlorinated molecules, which might be released in a final chlorination step.

(ii) Absorption of gaseous oxygen occurs statistically within the homologues, while isotopic enrichment may be a consequence of the volatility of the precursors.

(iii) The share of oxidation products formed directly from fly ash carbon must be higher for PCDF than for PCDD, assuming precursor structures containing ether bonds.

<b><sup>18</sup>O-Content</b>	Fly Ash MWI Göppingen	BCR-MWI Fly Ash	EPA-MWI Fly Ash
Gas feed: O <sub>2</sub>	91%	91%	92%
Emissions: CO/CO <sub>2</sub>	61%	50%	46%
<b>Dibenzofuranes</b>			
Cl <sub>4</sub>	59%	41%	40%
Cl <sub>5</sub>	57%	46%	43%
Cl <sub>6</sub>	66%	51%	49%
Cl <sub>7</sub>	65%	55%	51%
<b>Phenols</b>			
Cl <sub>2</sub>	40%	18%	29%
Cl <sub>3</sub>	68%	49%	47%
Cl <sub>4</sub>	79%	60%	66%
Cl <sub>5</sub>	83%	58%	68%
<b>Dibenzodioxins</b>			
Cl <sub>4</sub>	64%	35%	43%
Cl <sub>5</sub>	68%	39%	46%
Cl <sub>6</sub>	69%	46%	50%
Cl <sub>7</sub>	69%	50%	54%
Cl <sub>8</sub>	73%	69%	69%

Table 1) <sup>18</sup>O-contents of PCDD/F and chlorinated phenols compared with the gas feed

### 4 Conclusions

Chemisorbed oxygen of the residual carbon of MSWI fly ashes can be retrieved in large amounts in chlorinated products of thermal treatment. This outcome shows a direct participation of oxygen-containing carbon structures in the formation of PCDD and PCDF.

The formation of PCDF cannot simply be explained by condensation of chlorinated phenols, since the  $^{18}\text{O}$  content in chlorinated phenols is higher than in the supposed condensation products after loss of two HCl.

PCDD are either released directly from the residual carbon by oxidative breakdown or emerge from condensation of chlorinated phenols.

Higher chlorinated products are rather likely to be formed from volatile precursors, as they contain a higher share of oxygen from the gas phase. The oxygen transfer may occur at the reactive sites of the catalyst, where these products undergo further chlorination.

The online-monitoring of the gas phase composition reflects the fast adsorption of molecular oxygen - regardless of its isotopic content - at the starting point of the reaction. Afterwards, the release of  $\text{C}^{16}\text{O}_2$  can be observed, followed by  $\text{C}^{16}\text{O}^{18}\text{O}$  and  $\text{C}^{18}\text{O}_2$  with a delay of several minutes each. This outcome corresponds to the model of chemisorbed oxygen on the carbon surface, as it is found on activated charcoals: The first oxidation products to be trapped after heating are of natural isotopic consistency, while the carbon-bonded oxygen is gradually being replaced by the oxygen in the gas feed.

The data found are in good agreement with the results found by Olie et al.<sup>3</sup>, providing a better overview on gaseous and solid phase oxidation products and the influence of the residual carbon on fly ashes.

Showing the same tendencies in isotope specific oxygen incorporation, the different  $^{18}\text{O}$ -yields in  $\text{CO}$ ,  $\text{CO}_2$ , PCDD/F and chlorinated phenols of different fly ashes also reflect the influence of the carbon structure and its oxygen content.

### 5 References

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