

## Subcritical water degradation of dioxins

**I. Windal\*, S. Hawthorne<sup>#</sup>, E. De Pauw\***

\* *University of Liege, Mass Spectrometry Laboratory, B6c Sart-Tilman, B-4000 Liege, Belgium.*  
e-mail: I.Windal@ulg.ac.be

<sup>#</sup> *Energy and Environmental Research center, University of North Dakota, Grand Forks, North Dakota, 58202, USA*

### **Abstract**

**This paper investigates the degradation of dioxins in hot aqueous solution (200-300°C). Decomposition of native dioxins of different kind of fly ash samples, with different carbon content and with HCl pre-treatment or not, has been studied. Results show that both parameters have an importance on the degradation pathway and kinetics. The degradation of OCDD in pure water, and catalysed by fly ash has also been studied.**

### **Introduction**

Reaction in subcritical or supercritical water can be considered as environmentally friendly methods for the decontamination of polluted matrices. The dielectric constant of liquid water ( $\epsilon$ ) can be dramatically lowered by simply increasing the temperature under enough pressure to maintain the liquid state. At ambient temperature, water is too polar ( $\epsilon \approx 80$ ) to efficiently solvate low polarity compounds<sup>(1)</sup>. At 300°C,  $\epsilon \approx 25$ , and in supercritical conditions ( $T > 374^\circ\text{C}$  and  $P > 221$  bars),  $\epsilon \approx 5-15$ . Consequently, subcritical water (or hot water)- and supercritical water are effective solvents of organic compounds.

Grabel and al.<sup>(2)</sup> have studied the hydrothermal decomposition of dioxins and furans in hot aqueous solution. The degradation starts at 200°C and reaches 99% at 300°C after 1h in alkaline solution (NaOH 1M). A substitution of Cl by OH as well as a dechlorination/hydrogenation mechanism (which plays a minor role) have been established.

First experiments realized in our lab show that fly ash composition as well as HCl pretreatment have a big importance in the degradation pathway and kinetics.

### **Experimental section**

**1. Subcritical water degradation of native dioxins present in fly ash:** 2 g of fly ash were placed in a 64 mm long x 7 mm I.D cell with water previously purged with N<sub>2</sub>. The cell was closed (a 1ml head space of air remains in the cell) and heated in an oven to the desired temperature. After heating, fly ash and water were placed in a flat receptacle to evaporate the water. Dioxins are not soluble in water at ambient temperature, and are adsorbed on fly ash. Dioxins were then extracted by ASE (ISCO SFX-210) with toluene during 2h at 150°C, 50 bars, 1 ml/min. ASE performed in the same condition, but without any water treatment, was used as reference. Tetra-bromo-biphenyl and hexa-bromo-biphenyl, added after ASE, were used as internal standards in every experiment.  
**2. Subcritical water degradation of OCDD:** 1 g of OCDD contaminated glass beads (24 µg OCDD/g) was placed in the cell with water previously purged with N<sub>2</sub>. After heating, water and glass beads were extracted by liquid-liquid extraction with toluene. Hexa-bromo-biphenyl was used as internal standard. The same experiment was performed in triplicate without heating the cell to define the 100% recovery.

3. Analysis: The extracts were analyzed by GC- MS using a 30-m x 0.25 mm-i.d. HP-5 column. The two most abundant ions in the chlorine clusters of the molecular ion were recorded for each isomer of TCDD, PeCDD, HxCDD, HpCDD and OCDD (SIM). Two ions of the tetra bromo biphenyl and 2 ions of the hexa bromo biphenyl were followed too. The ratio between the 2 ions of each isomer was used to confirm the identity of dioxins or poly bromo biphenyl.

## Results and discussion

### OCDD as a model compound.

To investigate the effect of temperature on the destruction, Octachloro Dibenzo-p-dioxin was chosen as a model compound. Contaminated glass beads (24 µg OCDD/g) were placed with water in a closed cell and heated in an oven. After heating, OCDD were extracted by liquid-liquid extraction using toluene. Figure 1 summarises the results obtained at 200, 250 and 300°C. To identify degradation products, the extract was analysed by GC-MS in full scan mode. No compounds were detected except traces of tri and tetrachlorophenols, after 30 minutes at 300°C. According to these results, further investigations were performed at 300°C.

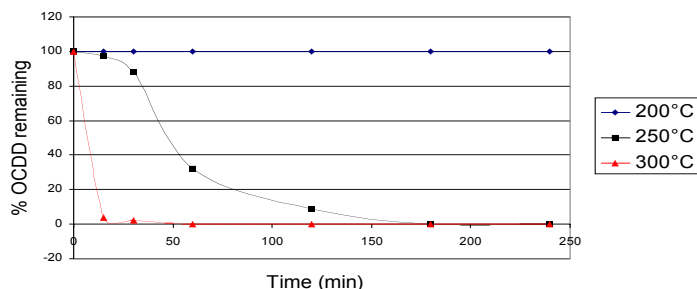


Figure 1: Hydrothermal decomposition of OCDD

The development of analytical methods for the analysis of dioxins in fly ash by Supercritical Fluid Extraction has already brought to light different dioxin behavior based on fly ash composition, and specially on the level of carbon<sup>(3)</sup>. Consequently, 2 kinds of fly ash with low or high carbon content were studied.

### High carbon content fly ash.

This fly ash sample was collected at the bottom of an electrostatic precipitator in a municipal waste incinerator, and is a mixture of dust coming from the combustion unit and of lime and activated carbon (4%) used for the fume purification system.

2 g of fly ash were placed in the cell with water and heated 2h at 300°C. The pH of water was 11, due to remaining lime used for the fume purification. The chromatograms of the extracts (without heating, and after 2h at 300°C) are shown in figure 2.

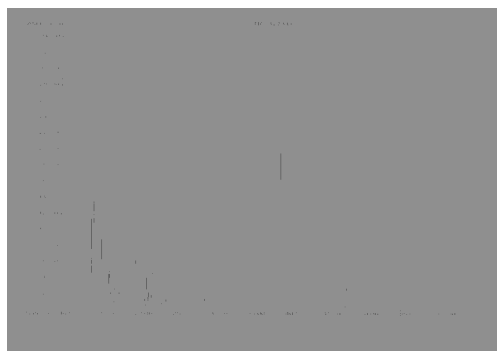
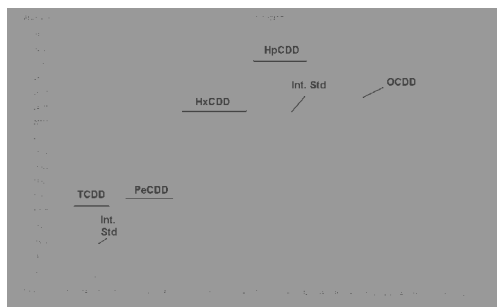
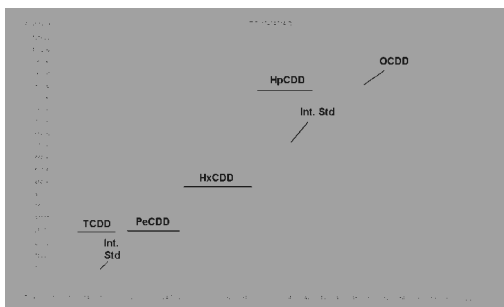


Figure 2 a : Chromatogram of the extract of fly ash without water treatment (SIM of dioxins). Figure 2 b : Chromatogram of the extract of fly ash after 2h in water at 300°C (SIM of dioxins). Int. Std: Internal standard.

Figure 3 a : Chromatogram of the extract of fly ash pre-treated by HCl (SIM of dioxins). Figure 3 b : Chromatogram of the extract of fly ash pre-treated by HCl, after 2h in water at 300°C (SIM of dioxins). Figure 3 c : Chromatogram of the extract of fly ash pre-treated by HCl, after 8h in water at 300°C (SIM of dioxins). Int. Std: Internal standard.

The concentration of all isomers decreases in the same way : about 70-80% destruction after 2h. No dioxins were detected after 8h of water treatment at 300°C.

The pre-treatment of fly ash by HCl prior to extraction greatly improves the percentage recovery of dioxin in SFE and Soxhlet extraction. A part of the matrix is dissolved and dioxins are more accessible for the extraction. Fly ash was then treated with HCl 1M during 2h and rinsed 3 times

with water before the experiments, to allow a better accessibility of dioxins for destruction. The chromatograms of the extract without heating, and after 2 or 8h at 300°C are shown in figure 3. The pH of water was 7 due to the rinses. The percentage of carbon is higher than in the non treated fly ash: 8,5%, as a part of the matrix is dissolved during the acidic treatment, and dioxins concentrated on a smaller volume. In this case, a dechlorination/hydrogenation reaction is well observed, with the formation of lower chlorinated dioxins as intermediates of reaction (the identity of dioxins were confirmed by high resolution GC-MS). The complete destruction of all isomers of dioxins is much slower. Another kind of fly ash pre-treated by HCl, and with a high carbon content (12% after acidic treatment) was also tested in these conditions, with the same observation of a dechlorination/hydrogenation mechanism.

To emphasise the effect of fly ash on the destruction, the following experiments were performed: in a cell were placed 0.5 gr of fly ash non treated, 40µg of OCDD and water. The cell was closed and heated 2h at 300°C. Fly ash was dried and extracted by ASE. No dioxins were detected in the extract. When the same experiment was performed with fly ash pre-treated by HCl, the dechlorination/hydrogenation mechanism was well observed (the lower chlorinated dioxins were detected at a concentration far above native dioxins present in the small amount of fly ash used, and result from the dechlorination of the OCDD, added in very high concentration). The dechlorination/hydrogenation mechanism seems to be favoured when fly ash pre-treated by HCl is present.

### Low carbon content fly ash.

The same experiments with a low carbon content ( 2,1% after acidic treatment) are under investigation. No dioxins were detected after 2h at 300°C when fly ash is pre-treated by HCl, which indicates that, at least, the kinetics are very different.

### Conclusions.

Dioxins were decomposed in every experiment conducted at 300°C, but mechanisms and kinetics vary greatly. When only water and OCDD are present (pH=7), the degradation is quite fast at 300°C. The dechlorination/hydrogenation reaction was not observed and no degradation products were identified (except once : traces of tri and tetra chlorophenols).

With the high carbon content fly ash, different mechanisms are involved if the fly ash is pre-treated by HCl (dechlorination/hydrogenation, pH=7) or not (pH=11).

The effect of pH is difficult to establish as different mechanisms were observed at the same pH. Reactions are faster if the carbon content of fly ash is lower.

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