

Thermal degradation of PCDD/F, PCB and HCB in municipal solid waste ash

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Abstract

A thermal degradation procedure for reducing the concentrations of mono- to octa-chlorinated PCDD/Fs, PCBs and hexa-chlorobenzenes (HCB) in filter ash from incinerated municipal solid waste (MSW) is described. Thermal treatment of filter ash samples at 500 °C for 60 min in a closed system providing low oxygen conditions resulted in 97% and 99% reductions in the total and I-TEQ concentrations of PCDD/Fs, to 6.8 µg kg⁻¹ ash and <0.05 µg I-TEQ kg⁻¹ ash, respectively. Increasing the thermal treatment time to 480 min, at the same temperature, yielded 99% reductions in both total and I-TEQ concentrations of the mono- to octa-chlorinated PCDD/Fs. Similar effects were observed for HCB and PCBs. The data from this study indicate that PCDD/Fs and other toxic organic compounds in ash from incinerated MSW, can be effectively degraded by this procedure, which combines relatively low-temperatures, short treatment times, and low oxygen conditions.

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1. Introduction

Municipal solid waste (MSW) can provide a significant energy resource, if it is incinerated, and the energy produced is recovered. In Sweden, 3.2 Mtonnes of MSW was incinerated during the year 2004, producing a total of 9.3 TW h of which 8.6 TW h was used for heating, and 0.8 TW h was used for electricity generation. However, the incineration process also generates solid residues, in the form of ash, which is associated with adverse environmental effects, due to its contents of toxic organic and inorganic compounds. The ash produced from MSW incineration can be divided into three different categories: bottom ash, fly ash and flue gas cleaning products. Bottom ash is the main ash fraction produced in a mass burn combustor and accounts for about 80% of the total flow, whilst

fly ash is the predominant fraction produced in fluidized bed combustors, accounting for 90% of the total ash flow.

In Sweden, mass burn combustors are the most commonly used for MSW, and bottom ash is, therefore, the predominant fraction, and the remainder consist of fly ash and flue gas cleaning products and mixtures of various ash fractions. Bottom ash is almost free from organic compounds, and is considered to be of no major environmental concern. However, fly ash and flue gas cleaning products contain significant quantities of toxic organic compounds, known collectively as persistent organic pollutants (POPs), which include polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs).

Depending on the type of air pollution control devices deployed, PCDD/Fs in fly ash can account for more than 90% of the total PCDD/Fs released from an incinerator. In Sweden, fly ash from MSW combustion is classified as hazardous waste, due to its content of PCDD/Fs and other POPs, heavy metals and water-soluble salts. For this reason fly ash must currently be disposed of in controlled landfills, but this is only a short-term solution as

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degradation of POPs in landfills is an extremely slow process. Moreover, current knowledge on the leaching of POPs during long-term storage remains rather limited. A concentration limit for PCDD/Fs in waste has recently been set in the European Union to $\sim 15 \mu\text{g TEQ kg}^{-1}$. Consequently, ash containing PCDD/Fs at concentrations above this limit will need to be treated in order to comply with the new regulations. Therefore, it is important to develop viable methods for effectively degrading PCDD/Fs in fly ash from MSW incineration, particularly as they may obviate the need to dispose of fly ash in landfills and reduce the cost incurred by commercial companies for landfill usage. Furthermore, the low levels of POPs in treated fly ash may allow this by-product of incineration to be used in new industrial applications.

The organic compounds in concern are thermally unstable; at high temperatures all organic compounds are decomposed. This has resulted in a number of methods where some methods are based on fusion and vitrification to render bottom and filter ashes inert. However, the high cost and energy demands associated with these processes have precluded their use on full industrial scale in EU countries. The Hagenmaier process is a low-temperature thermal process for decomposing PCDD/Fs in filter ashes that was developed in the early 1980s and consists of heating the ash to a temperature of 350–400 °C in a rotary drum under low oxygen conditions with a treatment time of 30 up to 60 min (Hagenmaier et al., 1987a; Ischida et al., 1998). However, its cost is of major disadvantages. Another process is the 3R Process which recovers fly ash and HCl from the flue gases and removes heavy metals from the fly ash by extraction with HCl. It returns a pelletized fly ash to the incinerator. Full scale experiments proved the thermal decomposition of PCDD/PCDF (Vehlow et al., 1990).

Degradation of PCDD/Fs is dependent on several factors, with temperature recognized as being the most important in determining whether formation or degradation is favoured. Thermal treatment time, atmosphere, and fly ash composition, have also been found to be important determining factors. Furthermore, in a recent study (Lundin and Marklund, 2005) the degradation of PCDD/F was found to be dependent on the composition of the fly ash, including its content of different metals, sulphur, carbon and calcium, as well as pH. Relatively low-temperatures, in the order of 300 °C, were also found to be sufficient for achieving a high level of degradation in a closed system. Similar observations have been reported in other studies (Vogg and Stieglitz, 1986; Hagenmaier et al., 1987a,b; Stieglitz and Vogg, 1987). The atmosphere in which thermal treatment takes place has also been found to be an important determining factor, with an oxidative atmosphere, higher temperatures (400–600 °C) are required for the degradation of PCDD/Fs (Vogg and Stieglitz, 1986). However, a combination of an inert atmosphere with relatively lower temperatures (300–400 °C) has been found to result in effective degradation (Stieglitz and Vogg,

1987; Addink et al., 1995). In the absence of a gas flow, the rate of formation is higher (Addink and Olie, 1995), possibly because the oxygen is not removed, and can participate in formation reactions. However, in our previous study using a sealed system (Lundin and Marklund, 2005) the oxygen was found to be consumed and degradation became the predominant reaction.

To our best knowledge, there are very few degradation studies of PCB. Stach et al. (2000) have found that for PCB more than 87% of the added compounds to fly ash decomposed at 260 °C and the detoxification (expressed as I-TEQ) was >99%. At 340 °C, the decomposition was even higher, with detoxification reaching 100%. In addition Weber et al. (2002) have shown that dechlorination at 3-, and 4-positions is favoured and that a temperature of 380 °C and treatment time of 1 h are sufficient to destroy PCDD/Fs and PCBs in fly ash.

Studies in which the degradation products of PCDD/Fs and PCBs have been investigated remain sparse, although Visez et al. (2004) and Visez and Sawerysyn (2005), have shown that PCBz can be formed when PCDD/Fs are degraded. In addition, PCBz was shown to be a degradation product of PCDDs during the thermal degradation of 2-chlorophenol catalyzed by CuCl_2 (Visez et al., 2004) and thermal treatment of 2-MCDD at 350 °C for 100 min resulted in the formation of PCDD, which was, in turn, degraded to PCBz and other compounds, including tetrachloroethylene, hexachloroethane and tetrachlorocyclopentenedione (Visez and Sawerysyn, 2005).

Studies of degradation and dechlorination of hexa-chlorinated benzenes (HCB) remain sparse. Stach et al. (1999) found that 65.7% of HCB were dechlorinated at 350 °C, with 4-h treatment, and that lower temperatures resulted in lower dechlorination. They also found that Cu, CuO and PbO were effective catalysts for HCB dechlorination.

In view of this background information, and since data from most previous studies have been derived from experiments with small amounts of fly ash (<3 g), the aims of the study reported here were to investigate the degradation of native compounds, mono to octa chlorinated PCDD/F, PCB and HCB in larger quantities of ash (200 ml or ~ 130 g), using a closed system and low oxygen conditions.

2. Experimental section

A filter ash from a MSW mass burning plant in Sweden was used in this study, and the mean value of three samples, taken from the same batch, was used. The plant has an incinerator with an effect of 65 MW and the capacity is 20 tonnes h^{-1} . NH_3 is added to decrease NO_x , active carbon and $\text{Ca}(\text{OH})_2$ are added before the fabric filter. To determine the temperature required for optimal destruction of PCDD/Fs, a series of samples from the same batch of filter ash, each weighing approximately 3 g were placed in sealed glass ampoules, then thermally treated for 1 h at the following temperatures: 300, 365 and 450 °C. The experimental matrix is shown in Table 1. The filter ash

3. Results

The untreated ash samples had a total PCDD/F concentration of $218.1 \mu\text{g kg}^{-1}$ ash, of which $71.3 \mu\text{g kg}^{-1}$ ash (33%) were mono- to tri-chlorinated PCDD/Fs, whilst $146.8 \mu\text{g kg}^{-1}$ ash (67%) were tetra- to octa-chlorinated PCDD/Fs. As shown in Table 1, PCDFs dominated over PCDDs for all congeners, with PCDFs accounting for 86% of the total PCDD/Fs. As also shown in Fig. 1, the di- to hexa-chlorinated isomers of PCDF were predominant, while the concentrations of mono- to octa-chlorinated PCDDs in the ash samples were $<5 \mu\text{g kg}^{-1}$ ash for each homologue. The concentrations of the highly chlorinated isomers of PCDDs exceeded those with a lower degree of chlorination. The I-TEQ concentration in the untreated ash samples averaged $3.2 \mu\text{g I-TEQ kg}^{-1}$ ash (Table 1).

In the experiments in which filter ash was treated in sealed glass ampoules none of the treatments resulted in total degradation of all the PCDD/Fs. At 300°C the total concentration of PCDD/Fs decreased somewhat (25%) relative to that of the untreated ash. At 365°C the total concentration of PCDD/F decreased further (60%) to $87.3 \mu\text{g kg}^{-1}$ ash. In addition, the profile changed, the more lightly chlorinated PCDD/Fs becoming more abundant than the highly chlorinated PCDD/Fs. A further increase in temperature to 450°C led to a further decrease in total concentration of PCDD/F (>99%), to $1.5 \mu\text{g kg}^{-1}$ ash. The profile was not significantly different from that obtained by treatment at 365°C . The I-TEQ concentration were considerably decreased by treatment at 365°C (to $0.1 \mu\text{g I-TEQ kg}^{-1}$ ash) and 450°C (to $<0.05 \mu\text{g I-TEQ kg}^{-1}$ ash), but treatment at 300°C left it unchanged (Table 1). Therefore, since treatment at 450°C for 60 min was not sufficient to degrade all the PCDD/Fs present, and larger volumes were to be treated, we choose a temperature of 500°C for our subsequent experiments.

Quenching the ash after thermal treatment seems to have had no significant effect on the PCDD/F concentrations. The uncertainty in the measurements was 30% for the analysis. The data from the two quenched and non-quenched ash samples were therefore averaged and included in the results listed in this section and the Discussion. Increasing the treatment time to 480 min at 500°C decreased the total concentration of PCDD/Fs by more than 99% (Fig. 2). The increase in concentration at 120 min treatment compared to 90 min treatment was due to high concentrations of MoCDF (Table 1), which should have been in the same range as or lower than the 90 min treatment. The somewhat higher concentrations for the other isomers can be assigned to uncertainty of the analysis. The considerable reductions in I-TEQ concentrations, to less than $0.05 \mu\text{g I-TEQ kg}^{-1}$ ash after the treatment times used, indicates that detoxification was effective.

Even in the treated ashes samples PCDFs were present in higher concentrations than PCDDs (Fig. 2). Tetra- and penta-PCDFs were the most abundant isomers of the tetra- to octa-chlorinated PCDFs, followed by hexa-chlorinated isomers, whilst hepta- and octa-chlorinated isomers had similar concentrations to those of the PCDD isomers. The mono- to tri-chlorinated PCDD/Fs were dominated by PCDFs and the mono- to tri-chlorinated PCDDs were, in most cases, near their respective detection limits. In the treated ash samples, mono-chlorinated PCDF was the dominating congener, followed by di- and tri-chlorinated PCDF (Table 1). The same pattern was observed for mono- to tri-chlorinated PCDDs (Table 1).

Considerable reductions (>96%) in the total concentrations of PCDD/Fs were observed following treatment for the shortest time used (60 min), but the longer (480 min) treatment time resulted in an even larger decrease (>99%) (Fig. 2). Treatment for all tested times resulted in the degradation of PCDFs to a lesser extent than PCDDs. The

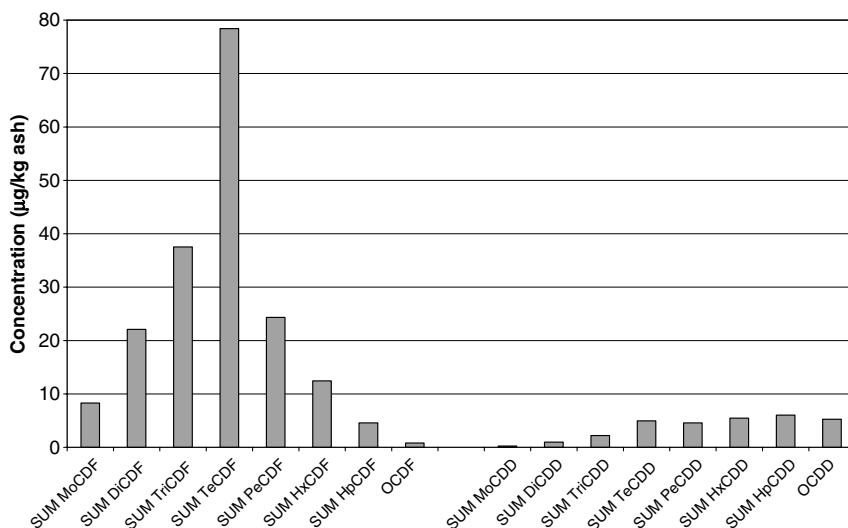


Fig. 1. Profile of PCDD/Fs in the untreated ash sample.

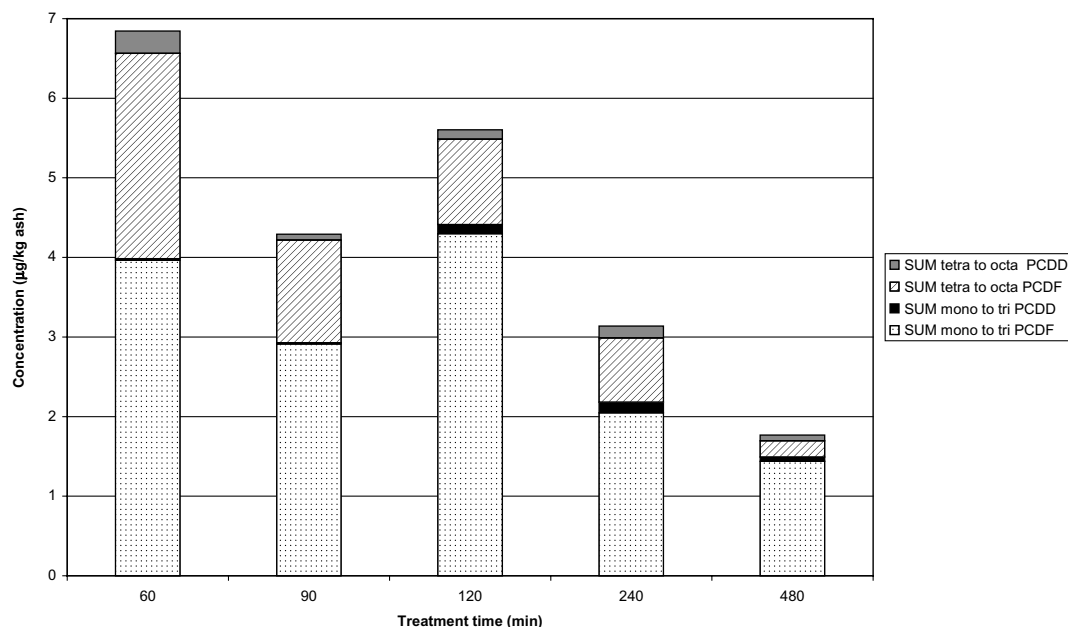


Fig. 2. The effect of different thermal treatment times on the total concentrations of PCDD/Fs and the sum of mono- to tri- and tetra- to octa-chlorinated PCDD/Fs in ash samples treated at 500 °C.

concentrations of the mono- to tri-chlorinated PCDD/Fs did not decrease to the same extent as those of the tetra- to octa-chlorinated PCDD/Fs. More than 99% of the tetra- to octa-chlorinated PCDDs were degraded by all but the shortest treatment (60 min). However, the longest treatment tested (480 min) was required to degrade tetra to octa chlorinated PCDFs to the same level.

The concentrations of PCBs were determined in five non-quenched samples, treated for 60, 90, 120, 240 and 480 min, respectively. Measurable concentrations of PCBs were found in the untreated ash sample (Table 2, Fig. 3a). The most abundant isomers were #77 ($0.8 \mu\text{g kg}^{-1}$ ash) and #126 ($0.7 \mu\text{g kg}^{-1}$ ash), both of which are planar PCBs (Fig. 3a). For all other isomers the concentrations ranged from 0.03 to $0.3 \mu\text{g kg}^{-1}$ ash. Ash samples treated at 500 °C showed decreases in their PCB concentrations. As the treatment time increased, PCB concentrations decreased irrespectively of the degree of chlorination. Treatment for 60 min resulted in more than 90% degradation of the majority of the PCBs (Fig. 3b), whilst a treatment time of 480 min increased the extent of degradation to more than 97%. However, there were some exceptions, as shown in Fig. 3c. After treatment for 120, 240 and 480 min, the lightly chlorinated PCBs were the most abundant, concentrations of the more highly chlorinated isomers, with 6–10 chlorine atoms (except #138 and #153), were below their respective detection limits.

The concentrations of HCB were determined in all samples, and as for the PCDD/Fs, the data from the two quenched and non-quenched ash samples were averaged and included in the results listed in this section and the Discussion. The untreated ash sample had a HCB concentration of $59.7 \mu\text{g kg}^{-1}$ ash and the concentrations were

Table 2

The concentrations ($\mu\text{g kg}^{-1}$ ash) of the different PCB isomers in relation to treatment time

<i>T</i> (°C)	–	500	500	500	500	500
<i>t</i> (min)	–	60	90	120	240	480
Quenched	–	no	no	no	no	no
No. of samples	1	1	1	1	1	1
#28	0.1	0.05	0.04	0.04	0.03	0.04
#52	0.04	0.02	0.02	0.02	0.008	0.01
#77	0.8	0.2	1.1	0.1	0.03	0.02
#81	0.3	0.02	0.1	0.01	0.004	0.002
#101	0.09	0.02	0.03	0.03	0.02	0.01
#105	0.09	0.01	0.09	0.004	0.003	0.002
#114	0.03	0.001	0.01	n.d.	n.d.	0.001
#118	0.2	0.4	0.02	n.d.	0.006	0.005
#123	0.05	0.2	n.d.	n.d.	n.d.	n.d.
#126	0.7	0.04	0.7	0.02	0.01	0.001
#138	0.1	0.003	0.03	0.03	0.01	0.02
#153	0.04	0.02	0.02	0.02	0.01	0.01
#156	0.09	0.001	0.07	n.d.	n.d.	n.d.
#157	0.05	0.004	0.03	n.d.	n.d.	n.d.
#167	0.1	0.002	0.04	n.d.	n.d.	n.d.
#169	0.2	0.004	0.09	n.d.	n.d.	n.d.
#180	0.05	0.01	0.02	0.01	0.01	n.d.
#189	0.07	n.d.	0.02	n.d.	n.d.	n.d.
#194	0.05	0.004	0.03	n.d.	n.d.	n.d.
#206	0.2	n.d.	0.05	n.d.	n.d.	n.d.
#209	0.1	n.d.	0.03	n.d.	n.d.	n.d.

after the thermal treatment for 60, 90, 120, 240 and 480 min, 0.3, <0.2, 0.3, <0.5 and <0.1 $\mu\text{g kg}^{-1}$ ash, respectively. After treatment at 500 °C for 480 min 99.9% degradation was achieved. Even treatment for 60 min resulted in degradation of >99%.

The analysis of the untreated filter ash sample revealed high levels of enrichment with inorganic compounds such

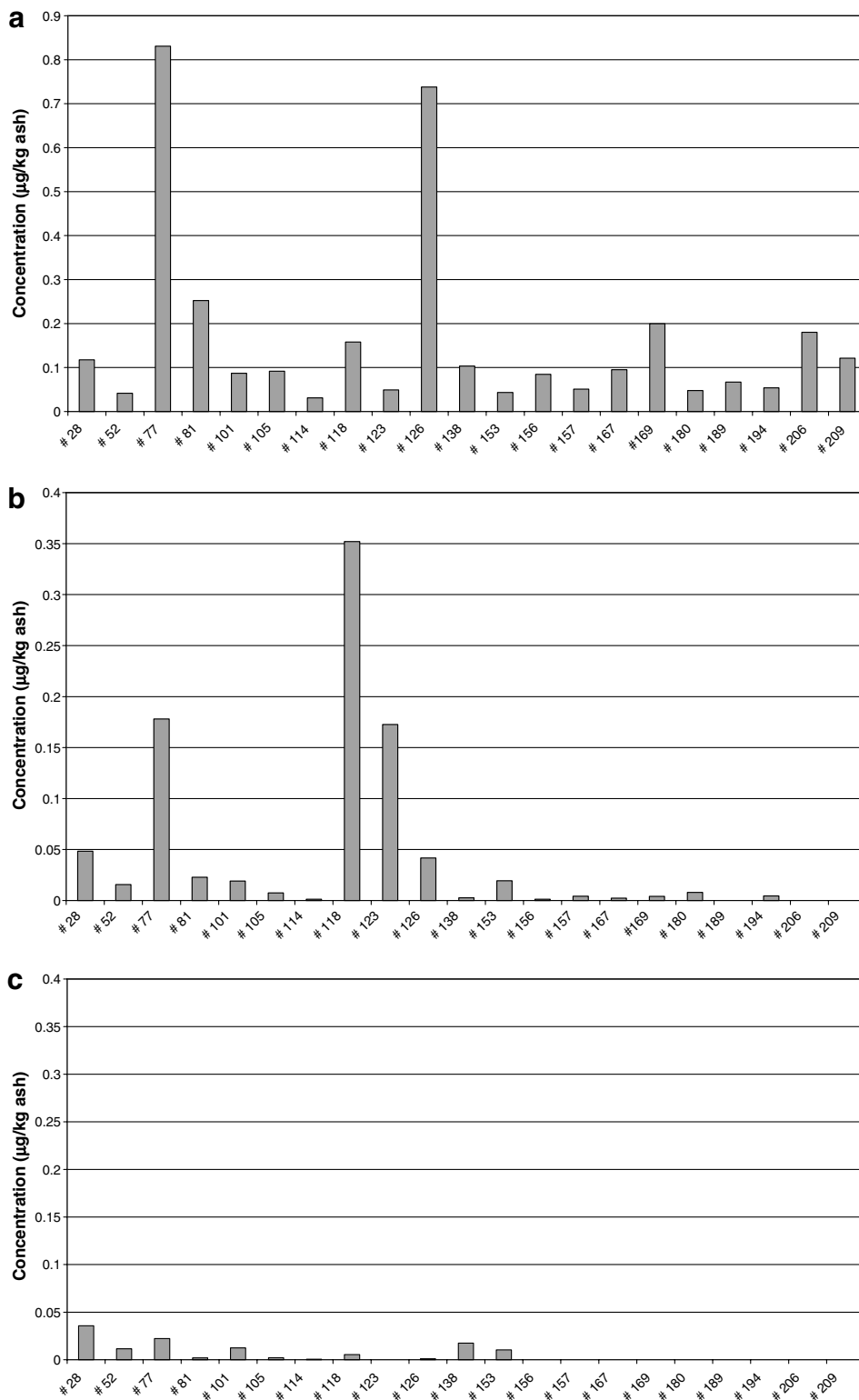


Fig. 3. Profile of PCBs in (a) untreated ash samples, and ash samples treated at 500 °C for (b) 60, and (c) 480 min.

as CaO, S and Zn with concentrations of 25.2%, 44000 mg kg⁻¹ and 37800 mg kg⁻¹, respectively. Other elemental species found, and which can catalyze the degradation of PCDD/Fs included Cu, Cd, Ni, Sn, and Pb with

concentrations of 1,270, 191, 97.6, 147, and 3420 mg kg⁻¹, respectively. The oxygen content was 1.7%. The analysis also showed that levels of oxygen were undetectable after 480 min treatment at 500 °C.

4. Discussion

A concentration limit for PCDD/Fs in waste has recently been set in the European Union to $\sim 15 \mu\text{g TEQ kg}^{-1}$, but is likely to be lowered in the near future. In this study, the I-TEQ concentration in the ash samples treated at 500°C was $< 0.05 \mu\text{g TEQ kg}^{-1}$ ash, which is appreciably lower than the limit. Furthermore, even in the untreated ash samples the I-TEQ concentration was also lower than this limit. Small quantities of ash treated at a temperature of 365°C for 60 min had I-TEQ concentrations that were also low ($0.1 \mu\text{g I-TEQ kg}^{-1}$ ash). However, PCDD/Fs were still present, and their total concentration was $87.3 \mu\text{g kg}^{-1}$ ash, of which 84% were mono- to tri-chlorinated PCDD/Fs.

With a temperature of 500°C and a treatment time of 480 min in a closed system, more than 99% degradation was achieved for all PCDD/Fs. The results show that tetra- to octa-chlorinated PCDDs were degraded to concentrations lower than $0.3 \mu\text{g kg}^{-1}$ ash after treatment for 60 min, whereas the degradation of tetra- to octa-chlorinated PCDFs to the same concentration required treatment for 480 min at the same temperature.

The relationship between formation and destruction in the presence of oxygen is described by the “dualistic principle” by Weber et al. (1999). The formation rate reaches a plateau at about 300 to 350°C while the destruction rate increases exponentially with increasing temperature. Under low oxygen conditions the destruction becomes the dominating force at lower temperatures, which was the reason for the greater degradation of PCDD/F in 500°C compared to 365°C . In addition the treatment time to achieve the same degradation is shorter.

The lightly chlorinated PCDD/Fs, i.e., those containing 1 to 3 chlorine atoms, showed the same degradation pattern as that observed for the more highly chlorinated PCDD/Fs. PCDDs concentrations were also very low ($< 0.2 \mu\text{g kg}^{-1}$ ash) after thermal treatment. However, longer treatment was required to degrade mono- to tri-chlorinated PCDFs, and even then their concentrations never fell to the low concentrations observed for PCDDs.

The higher chemical stability of PCDFs, compared to that of PCDDs may be a possible explanation for these contrasting observations. The closed-shell configuration of delocalized electrons, confirming to the Hückels rule of $(4n + 2) \pi$ electrons, confers aromaticity and, therefore, increases the stability of a PCDF molecule. However, in the case of PCDD molecule, this rule does not apply. When heat is applied, the thermal energy gained by the electrons of highly conjugated molecules causes them to reach an excited energy state, which increases their reactivity and, therefore, susceptibility to degradation or rearrangements. This probably explains the more rapid degradation of the PCDDs, compared to that observed for PCDFs. Similar observations were reported in a study by Visez and Sawerysyn (2005), who found that no detectable PCDDs remained after thermal treatment, while 30% of PCDFs were still

present. However, the concentration of PCDFs was higher than that of PCDD in untreated ash, with the mono- to octa-chlorinated PCDF accounting for 86% of the total amount of ($218.1 \mu\text{g kg}^{-1}$ ash) of mono- to octa-chlorinated PCDD/Fs. This also contribute to the more rapid rate of degradation of PCDDs, compared to PCDFs, since the more highly chlorinated isomers were not only destroyed but also formed lightly chlorinated PCDFs (by dechlorination), which in turn were destroyed or dechlorinated.

Due to the low PCDD concentrations, the I-TEQ concentrations were low ($< 0.05 \mu\text{g TEQ kg}^{-1}$ ash) for all treatment times and did not vary to the same extent as the total concentration of mono- to octa-chlorinated PCDD/F, due to that the lightly chlorinated PCDD/Fs do not contribute at all, and to the higher contribution of tetra- to octa-chlorinated PCDDs to I-TEQ concentration, compared to that of PCDFs. A further decrease in the concentration of tetra- to octa-chlorinated PCDF would lower the I-TEQ concentration even more. These results indicate that for PCDFs, the degradation process involved a combination of dechlorination and destruction. However, for PCDDs, no firm conclusion can be drawn as to whether degradation was due to dechlorination and/or destruction, particularly in view of the very low concentrations of all the PCDD congener (mono- to octa-).

As for the PCDD/Fs, it was the highly chlorinated (hexa- to deca-) PCBs that were degraded to concentrations below their detection limits. This was also found by Stach et al. (2000), who only detected mono- to tri-chlorinated PCBs after treating fly ash at 340°C . However, in our study both tetra- and penta-chlorinated PCBs were present after 480 min of thermal treatment at 500°C . Moreover, although the mono- to tri-chlorinated PCBs were still present, their concentrations were considerably lower than in the untreated ash (Table 2). The most abundant isomer was PCB #28, whose concentration in the ash was $0.035 \mu\text{g kg}^{-1}$ ash. The dechlorination of PCBs has been observed to occur predominantly at the toxicological relevant 3- and 4-positions of the ring structure, resulting in detoxification of PCBs during an early stage of the dechlorination/hydrogenation process (Weber et al., 2002). The low concentrations of PCBs present after 480 min treatment at 500°C does not contribute to the TEQ concentration, based on the corresponding WHO-TEF, indicating that effective detoxification of PCBs had taken place.

Polychlorinated benzenes have been shown to be degradation products of PCDDs, but the yields of PCBz obtained from experimental degradation of PCDF have been extremely low (Visez and Sawerysyn, 2005). In our study, low concentrations of HCB were obtained after treatment at 500°C , indicating that HCB present in the untreated ash were degraded and that any that may have been produced from the degradation of PCDD/Fs would have been degraded. Dechlorination of HCB has also been reported by Stach et al. (1999), who found that 65.7% were dechlorinated at a temperature of 350°C after treatment for 4 h.

The thermal treatment of the ash had no effect on the concentrations of the metals. The low concentration of oxygen (<0.01%) after treatment in 500 °C for 480 min shows that most or all of the oxygen initially present in the tube was consumed during the thermal treatment process.

5. Conclusions

The results from this study showed that thermal treatment of ash is a viable method to detoxify fly ash from incineration of MSW. A shift in chlorination degree was observed for PCDD/F, and PCB as well as HCB was also degraded. The data obtained from this study provide evidence suggesting that large quantities require relatively short treatment time. Therefore, a closed system with a pipe externally heated with heat generated from the incineration process as the source of thermal energy for the degradation procedure, with an internally heated screw to enhance heat transfer and thus reduce the thermal treatment time, could provide a viable means for the degradation of PCDD/Fs, PCBs and HCB in ash produced from the incineration of MSW. Continuous mixing of the ash during thermal treatment may further improve heat transfer and accelerate the degradation of PCDFs, which, in turn would shorten the thermal treatment time required. The economical advantage lies in the use of existing heat from the combustion process as the source of thermal energy.

Acknowledgements

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