

THERMAL DEGRADATION OF PCDD/F IN MSW FLY ASH

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Introduction

Municipal solid waste (MSW) can be an energy resource if it is incinerated and the energy produced is recovered. However, the incineration generates solid residues, ashes, which contain toxic organic and inorganic compounds. In the European Union (EU), fly ash from MSW combustion is classified as hazardous waste because of its contents of PCDD/F and other toxic organic compounds, metals, and water-soluble salts. Therefore, fly ash is required to be deposited in controlled landfills, which is a short-term solution as degradation of persistent organic pollutants (POP) is extremely slow in landfills and our knowledge of leaching of toxic compounds during long-term storage is limited. In addition, the European Commission has stated a project where, among other things, limit values of 14 selected persistent organic pollutants (POPs) and classes, where PCDD/F is one, will be defined. This will lead to that ash with PCDD/F concentrations above the limit value has to be treated. A method to degrade the PCDD/F in fly ash, which is environmental friendly and cost effective, is therefore desirable, so that the need for deposition of fly ash from MSW combustion in landfills is minimized. This would also lead to new fields of application for fly ash.

The organic compounds in concern are thermally instable; at high temperatures all organic compounds are decomposed. Therefore thermal degradation is a suitable treatment method for PCDD/F and other organic compounds. Degradation of PCDD/F is dependent on several factors. Temperature has long been considered to be the most important factor determining whether formation or degradation is favoured, but variables such as residence time, atmosphere, and fly ash composition have been found to be very important as well¹⁻⁶. We have in a previous study⁷ shown, that degradation of PCDD/F is dependent on the composition of the fly ash, i.e. content of different metals, sulphur, carbon, calcium, and pH, and that relatively low temperatures (300 °C) can be enough in a closed system. In addition, we have shown⁷ that a sealed system is independent of atmosphere, since oxygen is consumed and degradation becomes the dominating reaction.

The aim of this study was to examine the degradation of PCDD/F in larger volumes of ash with respect to temperature and residence time in a closed system.

Materials and Methods

A filter ash from a mass burning plant was used in this study. The untreated filter ash was analyzed for PCDD/F and inorganic compounds. An average temperature of 500 °C (varied between 470 and 530 °C) were chosen for the destruction experiments. A pipe of stainless steel with a volume of 200 mL was used, and the weight of ash treated was approximately 130 g. Two experiments at each residence time were performed (60, 90, 120, 240 and 480 minutes). After the duration of the experiment the pipe was dipped in water to enhance the cooling, then half of the samples were quenched (pored in a glass jar with water). The quenched ashes were dried over night. Each experiment was performed individually.

The treated ashes were analysed for mono- to octa chlorinated PCDD/F. A Soxhlet-Dean-Stark extractor was used for extracting the compounds in question. For this, approximately 3 grams of ash were taken and thoroughly mixed with 20 grams of toluene washed sand. ¹³C-labelled internal standards and acetic acid were added and then extraction during 48 h with two portions of toluene (400 mL in total) was carried out. The extract obtained was concentrated and divided in three portions (one ½ and two ¼).

Clean up of PCDD/F commences by applying one half of the extract to a multilayer silica column and eluting with n-hexane. This fraction was concentrated and then further purified on a column with a mixture of AX21-carbon and Celite, which was first washed and then eluted with 40 ml n-hexane, 40 ml cyclohexane:dichloromethane (1:1 on a volume basis) and 40 ml toluene. The toluene fraction contained the PCDD/F and was concentrated to 40 µL of tetradecane after the addition of recovery standard. The PCDD/F was analyzed on GC-HRMS, in this study an HP 5890 coupled to a VG Fison Autospec.

Result and discussion

The untreated ash had a concentration of mono to tri chlorinated PCDD/F of 71.3 ng/g ash and the concentration of tetra to octa chlorinated PCDD/F were 173.8 ng/g ash (Table 1). PCDF dominated over PCDD for both the mono to tri, 67.9 over 3.4 ng/g ash, and tetra to octa chlorinated PCDD/F, 147.6 over 26.3 ng/g ash (Table 1). Figure 1 shows that the tri chlorinated isomers of PCDF and PCDD were the dominating ones and that they contribute to more than 50 % of the sum of mono to tri chlorinated PCDF and PCDD. Tetra to octa chlorinated PCDD isomers was present in the same range (5 ng/g ash) and the mono to tri chlorinated isomers had a concentration under 5 ng/g ash (Figure 1). PCDF were dominated by di to hexa chlorinated isomers (between 22 and 80 ng/g ash) (Figure 1). The mono, hepta and octa PCDF isomers were present in the same range as the tetra to octa chlorinated PCDD (Figure 1). I-TEQ concentration was 3.17 ng I-TEQ/g ash (Table 1).

Table 1. Concentration of PCDD/F (ng/g ash) in untreated and treated ashes at 500 °C at different treatment times.

T (°C)	---	500	500	500	500	500
t (min)	---	60	90	120	240	480
No. of samples	3	2	2	2	2	2
SUM 1-3 PCDF	67.9	3.97	2.91	4.30	2.05	1.44
SUM 1-3 PCDD	3.4	0.03	0.04	0.14	0.14	0.08
SUM 4-8 PCDF	147.6	4.30	1.64	1.79	2.01	0.31
SUM 4-8 PCDD	26.3	0.28	0.07	0.12	0.15	0.07
1-3 PCDD/F	71.3	4.00	2.95	4.43	2.19	1.52
4-8 PCDD/F	173.8	4.58	1.71	1.91	2.16	0.38
Total PCDD/F	245.2	8.58	4.66	6.34	4.36	1.91
I-TEQ	3.17	0.035	0.016	0.023	0.036	0.006

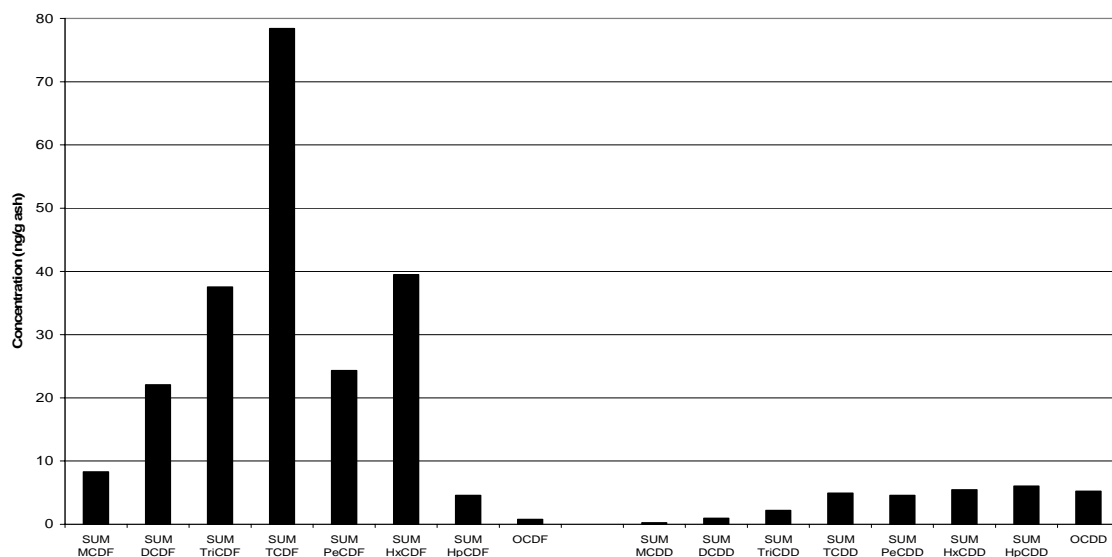


Figure 1. Concentration of mono to octa chlorinated PCDD/F in untreated ash.

Quenching the ash after thermal treatment seems to have no significant effect on the concentration of PCDD/F and therefore, the average of the quenched and unquenched samples were used for the results and discussions. Concentration of mono to octa chlorinated PCDD/F decreased with increasing treatment time. Mono to tri chlorinated PCDD/F decreased from 71.3 ng/g ash in untreated ash to 1.5 ng/g ash with a treatment time of 480 minutes, while the tetra to octa chlorinated PCDD/F decreased from 173.8 to 0.38 ng/g ash (Figure 2).

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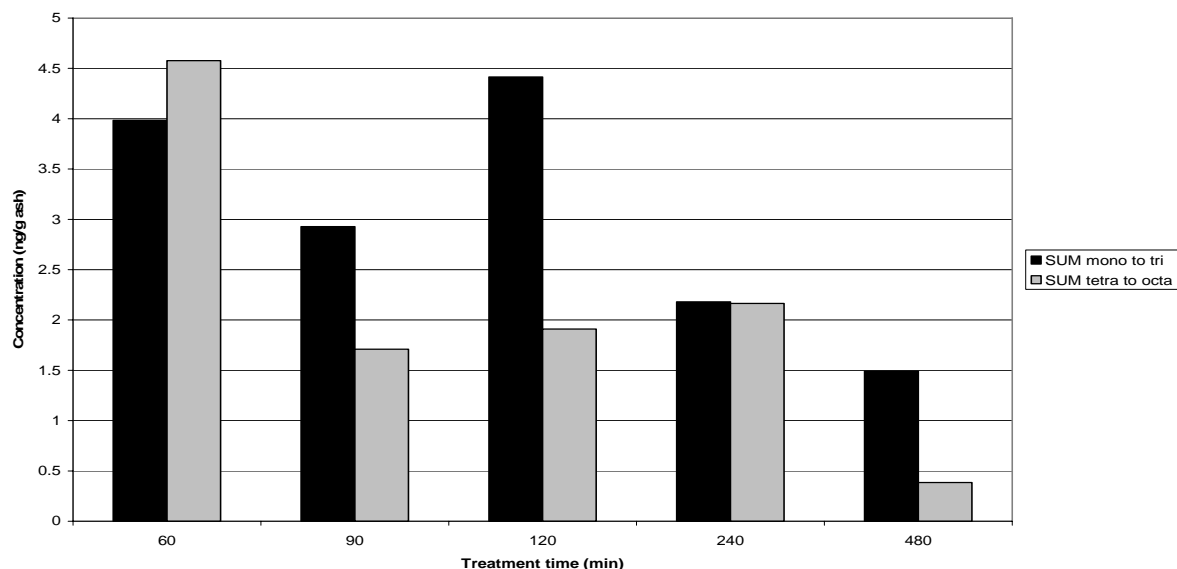


Figure 2. Concentration of mono to tri chlorinated PCDD/F and tetra to octa chlorinated PCDD/F in treated ashes at 500 °C at different treatment times.

We obtained an effective detoxification with respect to TEQ concentration already at 60 minutes and TEQ concentration were below 0.05 ng I-TEQ/g ash for all treatment times, and the lowest TEQ concentration were found at the treatment time of 480 minutes (Figure 3).

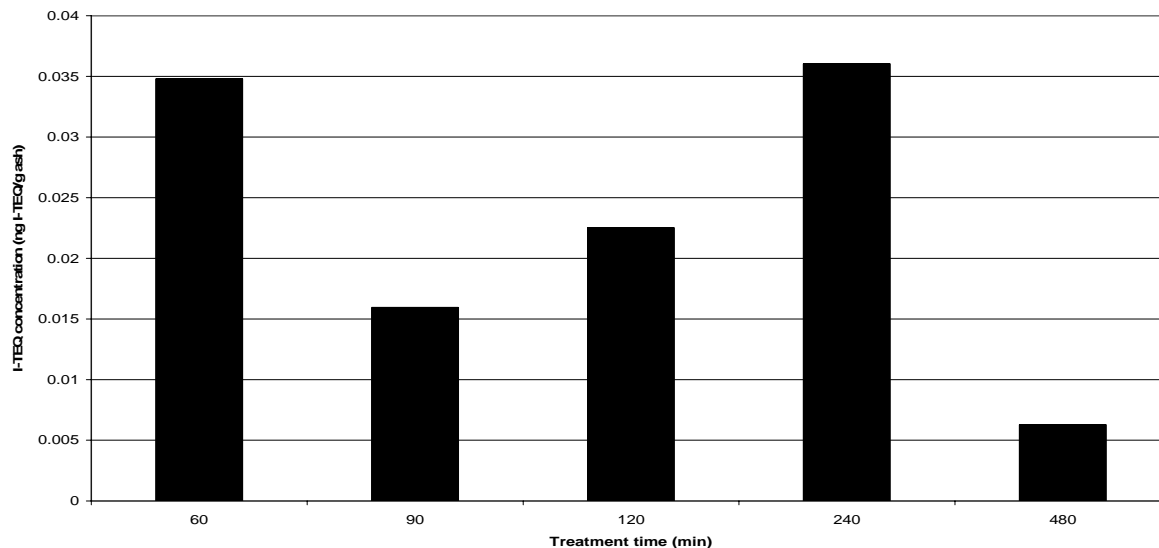


Figure 3. I-TEQ concentration in treated ashes at 500 °C at different treatment times.

Already at 60 minutes the concentration of tetra to octa chlorinated PCDD/F had decreased with more than 96 % and for mono to tri chlorinated PCDD/F the decrease was 94 %. The PCDD were degraded somewhat more than the PCDF. For tetra to octa chlorinated PCDD/F, PCDF were degraded with 96 % while PCDD were degraded with 98%. The corresponding degradation rates for the mono to tri chlorinated PCDD/F were 94 and 99 %. PCDD could not be detected in all experiments and if they were detected, the concentration was very low. PCDF were present in higher amounts, tetra and hexa PCDF were the most abundant isomers for the tetra to

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octa chlorinated PCDF, followed by penta chlorinated PCDF, while hepta and octa chlorinated PCDF were in the range of PCDD isomers. As for the tetra to octa chlorinated PCDD/F, the mono to tri chlorinated PCDD/F were dominated by PCDF and the PCDD concentrations were near detection limit with some exceptions. Mono chlorinated PCDF was the dominating congener followed by di and tri chlorinated PCDF in treated ashes while the opposite was true for untreated ash, the same pattern were observed for mono to tri PCDD.

The analysis of inorganic compounds shows that the filter ash was rich in CaO, S and Zn. Other compounds present that can catalyze the degradation of PCDD/F were Cu, Cd, Ni, Sn, and Pb. It also showed that after 480 minutes in 500 °C no oxygen was left in the ash. The thermal treatment of the ash does not affect the content of the metals. The somewhat higher concentration of C (4.65 and 4.15 % of dry substance) in treated ash could be assigned to that PCDD/F has been destroyed to smaller carbon molecules and the concentration of oxygen (<0.01 % of dry substance) shows that all oxygen in the tube were consumed.

The European Commission has stated a project where regulation on persistent organic pollutants (POPs) for the management of waste is the target. One of the four major objectives for this project are to propose specific concentration limits for the 14 POPs substances and substance classes above which the POPs content shall be destroyed or irreversibly transformed, and the suggested limit for PCDD/F in ashes is 1 ng TEQ/g ash. The TEQ concentration in our ashes treated at 500 °C (<0.05 ng TEQ/g ash) was well below this limit for all treatment times. With a temperature of 500 °C and a treatment time of 480 minutes in a closed system we achieved a degradation of more than 99 % for all PCDD/F. The results show that tetra to octa chlorinated PCDD was degraded to a concentration below 0.3 ng/g ash already at a treatment time of 60 minutes, whereas tetra to octa chlorinated PCDF required 480 minutes in 500 °C to reach below same concentration. The lower chlorinated PCDD/F (one to three chlorine atoms) followed the same pattern as the higher chlorinated PCDD/F, PCDD were present in very low concentration, less than 0.14 ng/g ash, after thermal treatment. However, mono to tri chlorinated PCDF required long treatment times to degrade, and they never reached the same low level that PCDD did. This can be assigned to that PCDF molecules are more stable and than PCDD molecule, due to a closed shell of delocalized electrons. The PCDF molecule is defined as an aromatic molecule, which the PCDD molecule is not since it does not fulfil the Hückels rule with $(4n+2)$ π electrons. When heat is added to a molecule, the electrons are excited, and result in an increase in energy level, which destabilizes the molecule, promoting degradation or rearrangements. Hereby, PCDD molecules were degraded faster than PCDF molecules. This was also shown by Wisez and Sawerysyn⁸ where no PCDD was left after thermal treatment, while 30 % was left of PCDF. However, the concentration of PCDF was higher than PCDD in untreated ash, the mono to octa chlorinated PCDF constituted 88 % of the total amount of mono to octa chlorinated PCDD/F, 245.2 ng/g ash. This also contribute to the fact that PCDD were degraded faster than PCDF since the higher chlorinated isomers not only were destroyed but also formed lower chlorinated PCDF, which in turn are to be destroyed or dechlorinated.

To summarize, PCDD/F were degraded already after 60 minutes. PCDD degraded faster than PCDF. With mixing during thermal treatment, heat transfer will be more effective and PCDD/F will probably degrade faster and treatment time could be shortened. PCB and polychlorinated benzenes will be examined in future work.

Acknowledgement

We gratefully acknowledge the financial support from the Swedish Association of Waste Management.

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