Low temperature thermal treatment of filter ash from municipal waste incinerators for dioxin decomposition on a technical scale

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Summary

In the temperature range of 250 to 400°C filter ash from electrostatic precipitators of municipal waste incinerators shows in the presence of air ("oxygen surplus conditions") a high potential of dioxin formation by *de novo* synthesis. The starting reaction of this *de novo* synthesis of PCDD/PCDF is a catalytic chlorine formation from metal chlorides in the presence of oxygen. We could demonstrate that filter ash also has a high catalytic activity of PCDD/PCDF decomposition which increases exponentially with temperature. In the temperature range of 250 to 400°C the rate of PCDD/PCDF formation in the presence of oxygen is greater than the PCDD/PCDF destruction. If, however, the PCDD/PCDF formation is limited by supression of chlorine formation due to a limited supply of oxygen ("oxygen deficiency conditions") the PCDD/PCDF concentration in filter ash can be reduced drastically by treatment in the temperature range of 300 to 400°C. This catalytic decomposition is not limited to dioxins. Other chlorinated aromatic compounds are decomposed as well.

The feasabilty of a technical application of this low temperature treatment of filter ash for reduction of dioxins and related compounds has now been tested on a 300 to 700 kg/h scale, corresponding to 20 to 40 tons of waste incinerated per hour. Reductions of PCDD/PCDF by 98% could be obtained during a 24 h test run. PCBs, chlorobenzenes, chloronaphthalenes and chlorophenols were reduced to the same degree. Total extractable chloroorganics were also reduced to 95%.

This treatment facility is installed at the municipal waste incinerator at Stuttgart.

Introduction

The amount of PCDD/PCDF emitted into the environment through solid residues of waste incineration is estimated to be currently by an order of magnitude higher than that emitted through the stack. It will be even higher if secondary measures for further reduction of stack emissions are based on adsorptive techniques.

At the 6th International dioxin symposium at Fukuoka we reported on the catalytic low temperature decomposition of PCDD/PCDF and related compounds on filter ash under "oxygen deficiency conditions" [1,2].

When in pilot plant studies (60 kg/h) PCDD/PCDF reductions of 95% could be demonstrated [3,4], a full scale treatment facility for electrostatic filter ash of the municipal waste incinerator (MWC) at Stuttgart was planned. It was finally installed at the end of 1989 and we want to report the results of the first continuous tests in March 1990.

Technical Concept

The results from the pilot plant study were encouraging enough that it was decided to build a full scale demonstration plant for the decontamination of PCDD/PCDF containing electrostatic precipitator ash on the technical principle of the pilot plant. In the fall of 1989 the facility was installed at the MWC of Stuttgart close to the electro filters in oder to use the temperature of the filter ash at this point.

The demonstration facility is designed to treat the precipitator ash of two furnaces (capacity 20 t/h for each furnace) in a continuos operation (maximum 1100 kg/h). The facility consists of a heated continuous flow mixer, 5 m long and 1.2 m in diameter, which is sealed off against atmospheric oxygen (Figure 1). The system is electrically heated in

three zones. The transport of the ash from the electrostatic precipitator to the continuous flow mixer is carried out by tube screw conveyors. To obtain an even distribution of the temperature of the ash and to aid the heat transfer the filter ash is thoroughly mixed by a rotor equipped with blades. After the ash has passed the heating zone it is cooled to below 140 °C. In order to obtain an air-tight system rotary air locks are installed in the ash transport system.

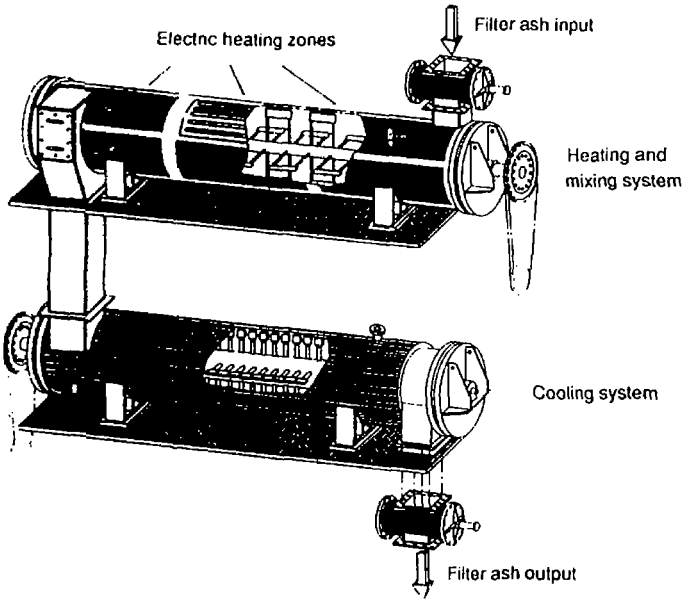

Figure 1: Filter ash treatment facility consisting of electrically heated continoous flow mixer and cooling system

Continuous test

In March 1990 the ash decontamination facility was undergoing a continuous test. During this period first the electrostatic precipitator ash of one furnace was treated (300-400 kg/h). During 24 h every hour a sample of untreated and thermally treated ash was sampled. Later the ash of the second furnace was also thermally treated (together 500-700 kg/h). Again samples of treated and untreated ash were sampled every hour for 24 h.

When the ash of one furnace (furnace 27) was treated the measured ash temperature was about 400°C with a residence time of about 2 h. The O_2 content in the continuos flow mixer was <1% and the rotor had 6 rpm.

When the ash of both furnaces (furnace 27 + 28) was treated the ash temperature decreased to about 370°C and the residence time decreased to 2 h.

In the mixer the pressure was slightly below atmospheric pressure.

Analytical procedure

10 samples each of thermally treated and corresponding untreated ash, evenly distributed over the 24 h test run with ash from furnace 27 were analysed for PCDD/PCDF content according to reference 5.

From the test run with ash from furnace 27+28 5 samples each of treated and untreated ash were selected for PCDD/PCDF analysis.

PCBs, tetra- to hexachlorobenzenes and chlorophenols were analysed by GC/MS using ^{13}C-labelled standards for quantification. Extractable organic chlorine was analysed by combustion in oxygen and coulometric determination of chloride.

Results and discussion

In Figure 2 the results for the PCDD/PCDF concentrations, expressed in toxicity equivalents according to NATO-CCMS, for corresponding samples before and after heat treatment are shown graphically. Table 1 shows some of the results in more detail. This table demonstrates that under appropriate conditions (conditions A) PCDD/PCDF concentrations can be reduced by more than 98%. More important than the decomposition calculated on a percent basis is the residual concentration obtained. This concentration is the real measure for the treatment efficiency and is more or less independant from the starting concentration. The higher the starting concentration, the higher will be the PCDD/PCDF reduction on a percent basis. The untreated filter ash in this study had lower than average PCDD/PCDF concentrations.

This study has shown that it is indeed possible to obtain residual PCDD/PCDF concentrations of less than 0.1 ng TE/g.

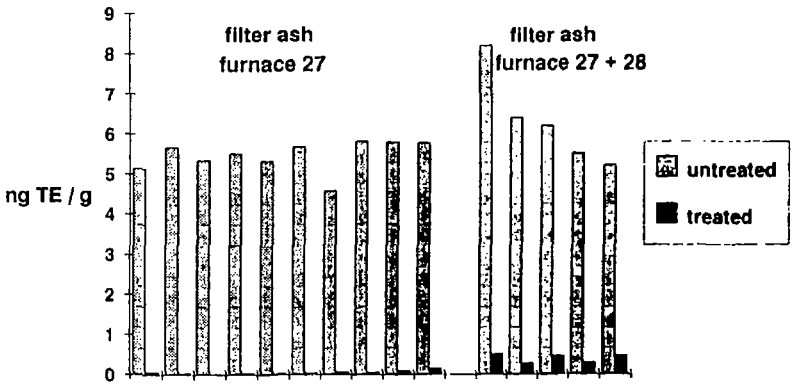

Figure 2: PCDD/PCDF content (toxicity equivalents (TE) according to NATO-CCMS) of electrostatic precipitator ash before and after thermal treatment under oxygen deficient conditions.

Table 1 also shows that after the heat treatment residual PCDF concentrations are higher than PCDD concentrations. This becomes more obvious when the average ash temperature becomes lower (conditions B, Table 1). This can be due to at least two different effects. Either the de novo formation of PCDF in presence of the residual oxygen is faster than that of PCDD or the decomposition by dechlorination is slower. A third possibilty is a faster chlorination reaction of PCDF than of PCDD which counteracts the catalytic dechlorination reaction. It is difficult to distinguish between these possibilities.

Further studies at this demonstration plant wil be carried out in order to optimize the heat transfer from the wall of the heated mixer to the ash. The goal is to reduce the PCDD/PCDF concentration for the higer ash load to about 0.1 ng TE/g of ash.

PCBs, tetra- to hexachlorobenzenes and chlorophenols were reduced to a similar degree as has been shown in detail for the PCDD/PCDF. The extractable organochlorine compounds also were found to be reduced to a similar degree.

A: ash from one filter

	untreated ash (n=10)			treated ash (n=10)			average
	min.	aver.	max.	min.	aver.	max.	reduction
	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	%
2,3,7,8-TCDD	0.15	0.32	0.46	0.002	0.005	0.012	98.4
Total PCDD	146	225	286	0.11	0.54	1.3	99.8
Total PCDF	131	176	236	1.1	3.0	7.8	98.3
TE (NATO-CCMS)	4.3	5.1	5.9	0,011	0.041	0.106	99.2

B: ash from two filter

	untreated ash (n=5)			treated ash (n=5)			average
	min	aver.	max.	min.	aver.	max.	reduction
	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	%
2,3,7,8-TCDD	0.2	0.26	0.32	0.018	0.038	0.05	85.4
Total PCDD	256	326	391	0.8	2.9	3.7	99.1
Total PCDF	118	152	210	13.5	19.3	25.2	87.3
TE (NATO-CCMS)	4.3	6.0	7.7	0.21	0.29	0.39	95.2

Table 1: Comparision of PCDD/PCDF content of treated and untreated filter ash. A : 400 kg/h, B : 700 kg/h

Conclusions

A full scale facility for the low temperature treatment of filter ash from MWCs has been tested for its efficiency of decomposing PCDD/PCDF and related compounds. High destruction efficiencies were obtained. Under optimum conditions residual PCDD/PCDF concentration of less than 0.1 ng TE/g (99% reduction) could be obtained. Other chlorinated compounds are reduced to a similar degree.

Low temperature treatment of solid residues from gas cleaning systems of MWCs can therefore be regarded as the current state of technology.

The tests described and the construction of the filter ash treatment facility at the MWC at Stuttgart was supported by the State of Baden-Württemberg.

References

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