FORMATION OF PCDD/F DURING START-UP OF MSWI

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Introduction

Since many years it is known from waste incineration that poor burnout quality of the flue gas correlates with high formation rates of PCDD/F. These early findings lead to an improvement of the design of the furnace geometry and the implementation of effective combustion control devices in modern municipal solid waste incineration plants (MSWI). By this optimization an almost complete burnout of the flue gas and hence much lower PCDD/F concentrations in the raw gas of about 1-2ng TEQ/Nm^3 during normal operation mode could be achieved.

But there are still some conditions of an uncompleted flue gas burnout in MSWI which still require an improvement and the development of efficient control strategies:

- malfunctions of the combustion system
- start-up and shut-down of the furnace

Several authors reported about high formation rates of PCDD/F [1-6] especially during start-up and shut-down procedures of the furnace. Although modern MSWI are run most of the operation time in a controlled mode and the time ranges for start-up and shut-down compared to the total running time are relatively short, the high amounts of PCDD/F formed during these conditions can lead to a not negligible contribution to the total annual PCDD/F emission of a MSWI [5].

To guarantee permanent low PCDD/F emission levels also at start-up and shut-down conditions one measure might be the improvement of the design of the flue gas cleaning device. In case of a catalytic process the result would be an over dimensioning of the apparatus for normal operation and the consequences are increased costs. Adsorption methods would transfer the problem to the residues. An alternative could be to prevent PCDD/F formation by primary measures like the improvement of the burner design/operation and/or the chemical inhibition of PCDD/F formation. Investigations by several authors [7-10] showed that PCDD/F formation could be lowered at increased SO_2 concentration in the flue gas.

To identify the major location of PCDD/F formation and also to quantify the potential of suppressed PCDD/F formation by the addition of sulphur to the fuel during start-up of MSWI special experiments were carried out at the pilot incinerator TAMARA [6].

Experimental

The maximum thermal capacity of the TAMARA furnace amounts to 500 KW. Start-up of the furnace usually takes place by igniting natural wood chips loaded on the grate with a natural gas burner (230KW) located above the grate in the middle of the length. When the temperatures inside the first flue reach 950°C the woodchips are replaced by municipal solid waste.

Two start-up procedures were investigated: one normal start-up (a) and a second one where sulfur pellets were added to the wood chips (b). Before starting the campaigns the combustion chamber, the flues and the boiler was cleaned well manually.

During both start-up experiments PCDD/F sampling was carried out in the flue gas downstream of the boiler. Beginning with the ignition of the gas burner sampling took place in two hours subsequent sampling intervals over a total duration of about 32 h. The major flue gas composition (O_2, CO_2, CO, Σ org. C (C_nH_m) by FID, SO_2, HCl, NO, H_2O) together with a number of temperatures inside the furnace were measured simultaneously.

Results

The measured data are depicted in Fig. 1. Both campaigns were started at 9 o'clock in the morning. As shown in the graphs (a.1) and (b.1) the temperature inside the first flue (ATM.T53151) reached nearly 1000°C at midnight, 15h after starting the burner. At this time the gas burner was switched off and the woodchips were replaced by municipal solid waste. This point in time is indicated by a steep increase of the HCl curve in the pictures (a.3) and (b.3).

During the first four hours of operation the temperatures inside the furnace were rather low and the burnout of the flue gas was uncompleted. High concentrations of products of incomplete combustion (PIC) could pass the combustion chamber as shown by concentrations of CO and Σ org. C (C_nH_m) in the plots (a.2) and (b.2). The maximum concentrations of CO exceeded the measuring range (1000 mg/Nm^3) of the CO analyzer and the maximum concentrations of the hydrocarbons rose up to about 2g/Nm^3. The soot concentrations in the flue gas showed the same trend. Seven hours after starting the furnace, the temperatures were high enough to complete the burnout of the flue gas and the concentrations of PICs dropped down below the detection limit.

Looking at the concentrations of PCDD/F in the flue gas shown in the plots (a.4) and (b.4) it is obvious that in both experiments the maximum concentrations were found four to six hours after start-up. The peak concentrations of PCDD/F occurred 4-5 hours delayed compared to the maximums of the CO and the hydrocarbon curves. At the time when the highest PCDD/F formation rates were detected the burned fuel contained only trace amounts of chlorine as obvious looking to the HCl curves of the plots (a.3) and (b.3). Furthermore, the fuel change from wood to waste had no effect on the formation rates of PCDD/F. This findings can only be explained by the inherent presence of chlorides on the surfaces of the flues and the boiler. These chlorides together with removed soot particles (and condensed hydrocarbons) from actual start-up must have caused the formation of PCDD/F by de-novo synthesis [11)] when the local temperatures exceeded 200°C. The chlorine contamination of the furnace walls and boiler surface together with the fresh deposited soot particles lead to PCDD/F formation. This reaction took place over a very long time even when the combustion was efficient and the flue gas burnout was practically complete. This fact is well known as "Memory effect" [6, 12)].

The comparison of the campaigns with normal start-up (a) and the start-up with sulfur addition to the fuel (b) showed that temperatures and concentration curves of PICs were nearly identical. The sulfur addition (b.3) resulted in high levels of SO_2 in the flue gas. The increased SO_2 concentrations at the experiments (b) lead to significant lower total PCDD/F formation as shown in Fig. 2. The figures depict the total amounts of PCDD/F, hydrocarbons and soot integrated over the whole duration of 32h. While in both campaigns the total formation of PICs were comparable the sulfur addition caused a decrease of PCDD/F formation by a factor of three.

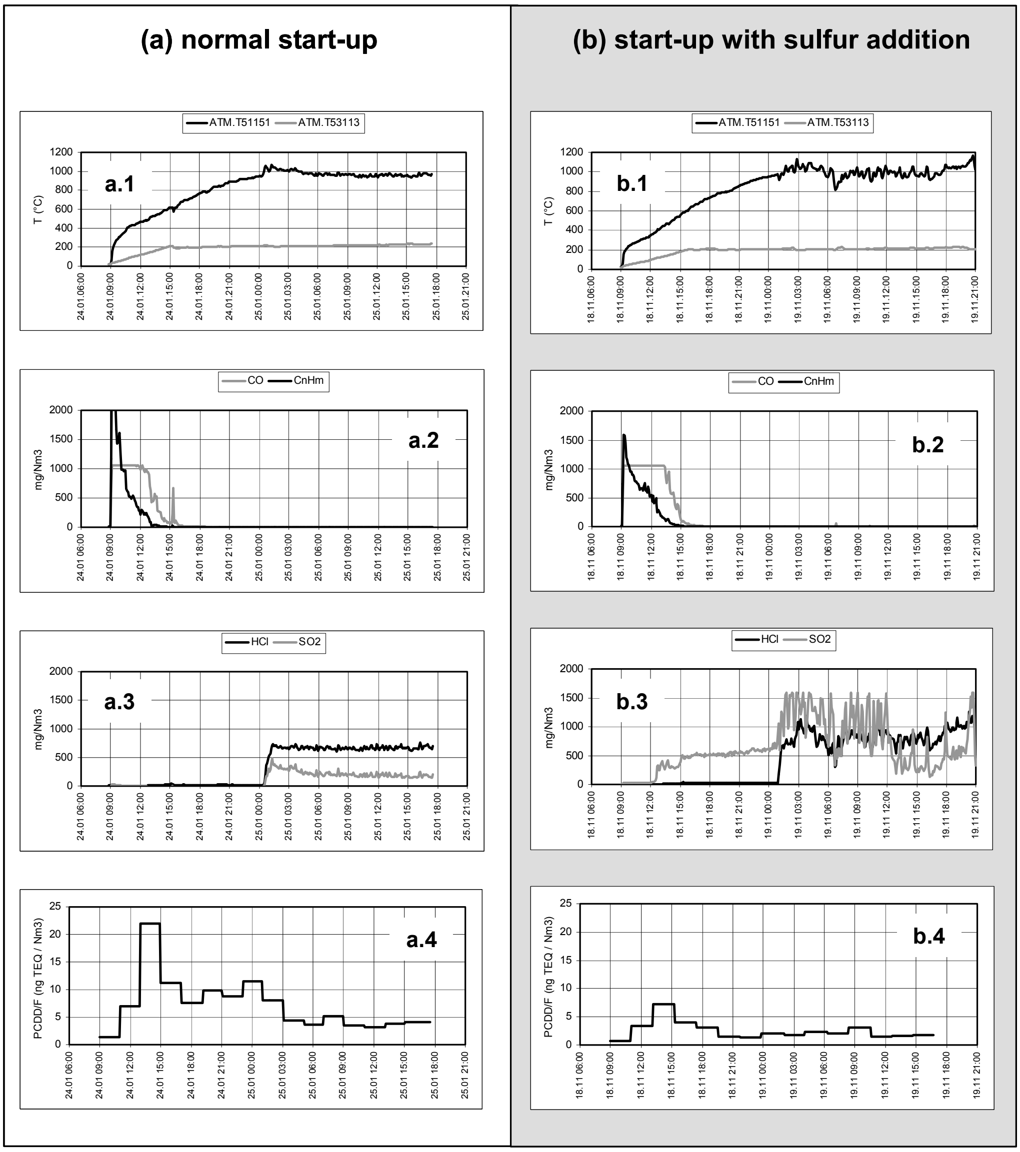

Fig.1: Time plots of temperatures, CO, C_nH_m , HCl, SO_2 and PCDD/F during start-up

Summary and Conclusions

The investigations showed that PCDD/Fs were formed in large amounts during start-up of a MSWI caused by ineffective combustion conditions. At the beginning of the start-up the temperatures of the furnace were rather low and soot particles as well as hydrocarbons were able to pass the “cold“ combustion chamber and to contaminate the surfaces of the flues and the boiler. In this locations chlorides were still present. In practice these chlorides cannot be removed completely by cleaning. The progressive increase of the temperatures at these locations caused PCDD/F formation by de-novo synthesis (>200°C) from the separated carbon species in combination with the chlorides over a long duration. Furthermore the experiments document that increased concentrations of SO_2 in the flue gas can reduce PCDD/F formation during start-up.

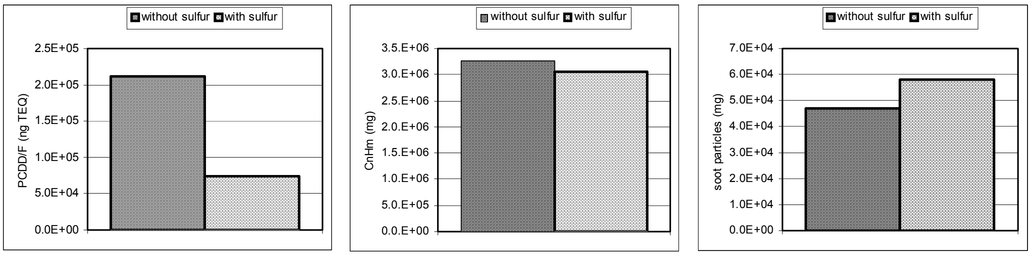

Fig.2: Total formation of PCDD/F, C_nH_m and soot (integration over 32 h since start)

To minimize PCDD/F formation during start-up following recommendations can be given:

- Heating up of the furnace to high temperatures exclusively by a well adjusted burner.
- Start of solid fuel feeding not until the temperatures of the furnace are sufficient high.
- The combustion gases from the solid fuel during ignition should pass the flame region (optimized arrangement of the burner)
- Use of heavy oil (high sulfur content) for the burner operation or addition of sulfur to the fuel during start-up.

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