CONTROL OF PCDD/F FORMATION UNDER CONDITIONS OF FLUCTUATING COMBUSTION PERFORMANCE IN MSWI

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Abstract

In municipal solid waste incineration plants the heterogeneous composition of MSW leads to fluctuations of the burnout efficiency of the flue gas even during controlled combustion. Regions inside the post-combustion zone with oxygen deficiency or low temperatures result in strains of unburned flue gas containing significant amounts of CO, C_nH_m, and soot particles. Soot particles passing the post-combustion zone unburnt are partly deposited on the boiler surface together with chlorides-containing fly ash and lead to PCDD/F formation by de-novo synthesis at temperatures above 200°C. Detailed investigations revealed that short-term transient combustion conditions in the one-minute range already may cause a significantly enhanced PCDD/F formation. According to time-resolved measurements, PCDD/F formation is not directly correlated to the actual combustion situation. "Memory effects" after short-term sooting conditions promote the PCDD/F formation over a very long time.

In order to improve MSW incineration by optimizing the flue gas burnout, new methods for online monitoring of the burnout situation over the whole cross section of the post-combustion zone were developed and successfully tested in full scale. High burnout quality with minimized or even avoided fluctuations can be ensured by implementing these technologies in advanced combustion control systems, thus preventing PCDD/F formation.

Introduction

Today, municipal solid waste (MSW) is mainly burnt in grate furnaces. The emission of many pollutants as well as the bottom ash quality are subject to strict regulations. Despite the successful improvement of the combustion process during the last years, complex and expensive air pollution control systems are still necessary to comply with the emission limits. If it would be possible to efficiently suppress the formation of pollutants particularly of PCDD/F and NO_x by economic primary methods, the efforts in flue gas cleaning could be reduced significantly. Such primary measures must act selectively and be in compliance with all other aspects of an optimized waste incineration process [1].

At the DIOXIN conference 2006, we reported that at permanently low HCl/SO_2 ratios (Cl/S ≈ 1-2) in the flue gas during a steadily efficient flue gas burnout (CO ≈ 2mg/Nm^3, TOC of the fly ash <0.1%), the formation of PCDD/F can be suppressed down to values of <0.1 ng/Nm^3 TEQ in the flue gas upstream of the flue gas cleaning system already [2]. The high levels of SO_2 were generated in an economic way by a process-integrated SO_2 cycle without any co-combustion of additional sulfur or sulfur compounds. High SO_2 concentrations caused a reduction of the chloride content of the fly ash by sulfation reactions resulting in very low Cl_2 formation rates inside the ash deposits on the boiler surface that guarantee very low PCDD/F formation rates as well as reduced boiler corrosion rates. These experimental investigations were demonstrated on the pilot scale at the TAMARA[3] grate furnace (thermal capacity 0.5 MW) when burning a crushed and well homogenized municipal solid waste delivered from a nearby MSW incineration plant. An efficient combustion of such a pretreated MSW can be achieved easily by minor efforts in combustion control only.

However, MSW generally is a very heterogeneous mixture of different materials varying widely in their chemical compositions and physical properties. In full-scale incinerators MSW is usually burned directly as collected without any pretreatment like an effective homogenization. This common practice at full-scale incineration plants results in more pronounced fluctuations of the local burnout behavior of the solid fuel bed over the grate area as well as during the flue gas burnout over the cross section of the post-combustion zone. Such transient combustion conditions can be compensated largely, but not completely by an optimized furnace design and complex process control systems. The tracking of the fuel feeding rate, the grate kinematics, and the air supply is accomplished automatically depending on the actual demand, based on online data from the monitoring of the O_2 level in the raw gas, the temperatures inside the combustion chamber, and the steam generation rate. Hence, incineration of an inhomogeneous MSW in full scale never is a stationary process. Insufficient mixing of the flue gas with oxygen at high temperatures results in strains containing small amounts of PICs (products of incomplete combustion = CO, C_nH_m and soot particles) leaving the furnace unburned. Soot particles, together with chloride-containing fly ashes, are partly separated on the boiler surface. At temperatures >200°C, PCDD/F formation takes place by oxy-chlorination reactions of the carbonaceous structures (soot) inside the ash deposits. This so-called de-novo synthesis [4, 5] is the predominant formation mechanism for the PCDD/F in the raw gas of MSW incinerators.

In order to transfer the above-mentioned technology of a “low-dioxin incineration process” from the pilot scale to full-scale application, it had to be investigated experimentally

- how PCDD/F formation is influenced by short-term fluctuations of the flue gas burnout efficiency
- and how combustion efficiency can be improved to ensure a steadily efficient flue gas burnout.

Experimental

The experimental investigations described below were carried out at a German full-scale MSW incinerator (grate furnace) and supported by much more detailed experiments at our TAMARA pilot plant.

The full-scale incineration plant has a designed waste throughput of about 20 t/h and a maximum thermal capacity of 50 MW. The plant has already been in operation for more than 20 years. The design of the furnace geometry remained almost unchanged all the time. Only the combustion process was improved some years ago by implementing a new process control system in order to meet the legal combustion regulations. Since this time, efficiency of the flue gas burnout has been ensured by keeping the flue gas temperatures at the end of the first flue gas duct at values of >850°C. The residence time of the flue gas in the area of the last port of the air supply and the position of the temperature measurement amounts to >2 s.

The whole experimental work at the full-scale plant took a period of about two months. The major flue gas constituents, such as CO, O_2, etc., were measured online, downstream of the boiler in front of the flue gas cleaning system. PCDD/F was sampled at the same location over time intervals of about 24 h.

The measurements revealed that under controlled combustion conditions, the average concentrations of CO in the raw gas always ranged well below the specified average emission limits of CO_{30min} <100 mg/Nm^3 and CO_{24h} <50mg/Nm^3. However, time-resolved evaluation of the data (Δt=10s) showed significant short-term CO peaks indicating fluctuations of the flue gas combustion performance. Similar effects were detected for the O_2 concentration. These findings were caused by the insufficient mixing of the high-calorific flue gas with the injected oxygen from the secondary air supply inside the post-combustion zone at high temperatures.

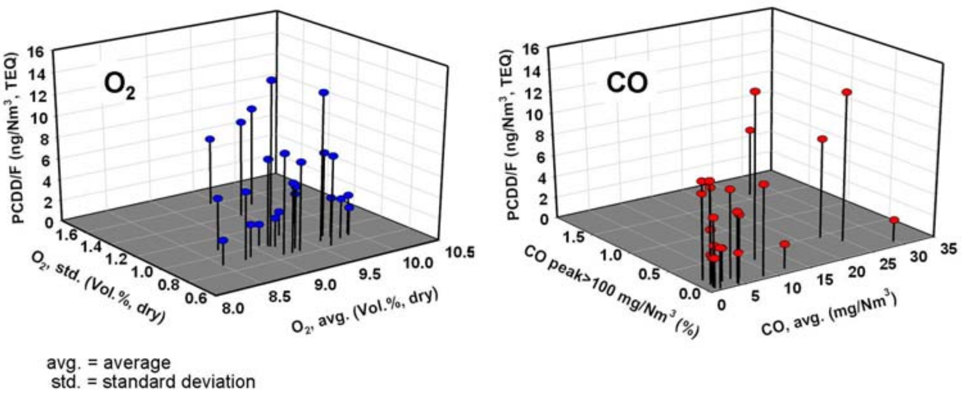

*Fig.1: PCDD/F concentrations as a function of **a)** the average value and standard deviation of O_2 and **b)** the average CO level and percentage of CO peaks.*

The PCDD/F concentrations found in the raw gas during the experimental campaign ranged from 2 - 15 ng/Nm^3 TEQ. No correlation between the dioxin level and the O_2 or CO concentration (averaged over 24 h) could be detected. The finding agreed well with results described in literature [6, 7].

A more detailed evaluation of the average O_2, standard deviation as well as average CO values, together with the amount of the short-term peaks >100 mg/Nm^3, is depicted in Fig. 1. The CO peaks were calculated as the percentage of total CO peak time in relation to total sampling time. A significant trend of the highest PCDD/F concentrations was found in the experiments with high standard deviations of O_2 and also in experiments with many CO peaks. On the other hand, "smooth combustion situations" characterized by low fluctuations of O_2 and hardly any CO peaks resulted in a relatively low PCDD/F formation down to values of about 2 ng/Nm^3 TEQ in the raw gas. This result indicates clearly that fluctuating combustion conditions lead to enhanced PCDD/F formation. Most modern MSW incinerators with well-designed furnace geometries supporting effective flue gas mixing at sufficient oxygen supply at high temperatures frequently exhibit such low dioxin concentrations in the range of 1-2 ng/Nm^3 TEQ close to the normal situation at TAMARA.

To gain a deeper insight in the reactions leading to enhanced PCDD/F formation during short-term transient combustion situations, several controlled experiments were carried out at the TAMARA pilot plant.

During and after the individual experiments, the temperatures and the flue gas composition were monitored online in the center of the flue gas duct about 1m downstream of the secondary air injection and also in the raw gas downstream of the boiler. Subsequently, PCDD/F sampling took place in the raw gas and at the end of the flue gas cleaning system (after fabric filter and two-stage wet scrubbing) in 1-2 h sampling intervals. At the raw gas position, the fly ash was additionally sampled. These filter samples were used for the determination of the TOC concentration and identification of the speciation of particulate carbon by using SEM.

A "cold combustion situation" was established by an excursive reduction of the fuel feed over a short time interval, keeping the air supply unchanged. The deficiency of fuel resulted in an increase of the O_2 level and cooling down of the furnace temperatures (Figs. 2 and 3, experiment "b"). As obvious from the figures, only a moderate increase of the CO concentrations ($\Delta t \approx 10$ minutes) and of the fly ash TOC was detected in this experiment "b".

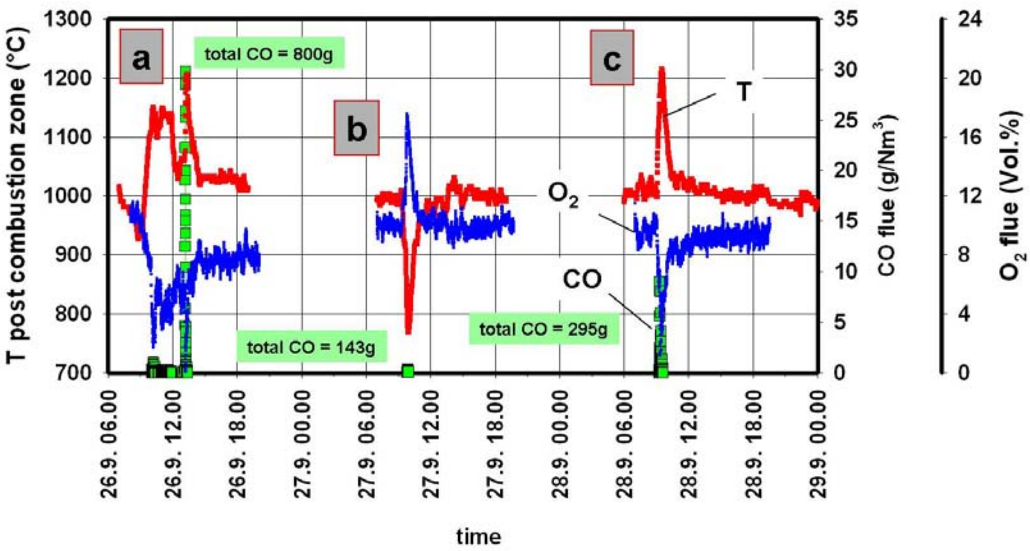

Fig. 2: Results of measurements in the center of the flue gas duct after secondary air injection.

Further experiments simulating oxygen deficiency conditions (Figs. 2 and 3, exp. "a" and "c") were carried out by an impulsive addition of a defined amount of a high-calorific fuel (polypropylene), while keeping the air supply constant again. These so-called "hot CO" situations in particular were characterized by a significant increase of the combustion temperatures up to 1200°C, while the local O_2 concentration dropped down close to zero. This situation caused a sharp short-term increase ($\Delta t \approx 1$-3 minutes) of CO up to very high peak concentrations in the center of the flue gas duct. The CO concentrations in the raw gas exceeded the end of the measuring range of the analytical equipment and the soot concentration simultaneously showed a temporary increase to rather high values.

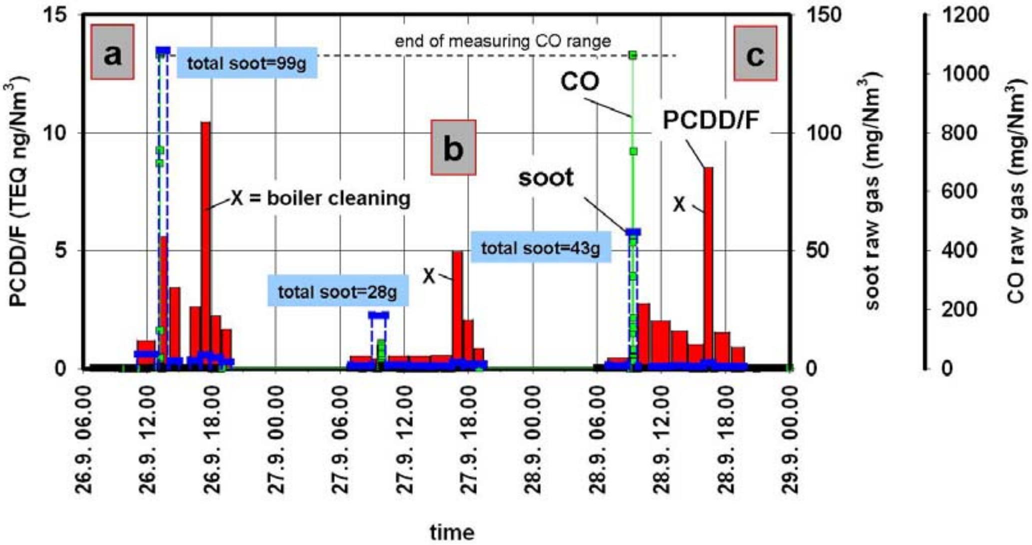

Fig. 3: *Results of raw gas samplings downstream of the boiler.*

The integrated total CO formation data measured inside the furnace were found to be well correlated to the total amount of soot particles detected in the raw gas. Thus, it was proposed to use CO as an easily online measurable surrogate for other PICs and particularly as indication of the soot particle concentration.

The poor flue gas burnout situations reflected by a short-term CO peak immediately lead to increasing PCDD/F concentrations in the raw gas (Fig. 3 “a” and “c”). After the combustion process returns to effective burnout conditions, the formation of PCDD/F remains at high levels for many hours, showing a slightly decreasing tendency with time only. Similar findings have also been described in literature [3, 8-10]. Comparing the results of all experiments (“a-c”), it was found that the quantity of PCDD/F formation was correlated positively to the amplitude of the respective sooting situation. Other chlorinated organic compounds like chlorobenzenes, particularly the highly chlorinated homologues (Cl_5- and Cl_6Bz), showed a behavior quite similar to that of PCDD/F.

During boiler cleaning (marked by “X” in Fig. 3), the PCDD/F level shows another significant increase. This well-known effect suggests the ash deposits in the boiler to be the source of PCDD/F formation.

The comparison of the raw and the clean gas PCDD/F concentrations during and after the short-term disturbance reflected a significant removal efficiency particularly of the highly chlorinated dioxins, while the chlorinated chlorobenzenes passed the flue gas cleaning system almost unaffected. The soot particles separated on the surface of the fabric filter improve the adsorption efficiency of the ash layer on the filter surface to an extent similar to that of flue gas cleaning technologies using carbon spray injection. Similar results were found by Weber [11]. As a consequence, the problem of enhanced PCDD/F formation during and after “sooting combustion” is transferred partly from the flue gas to the residues.

Discussion

The soot particles generated during the short-term disturbance were partly separated on the boiler surface and caused the enhanced PCDD/F formation over a very long time. These results demonstrate clearly that the PCDD/F concentration in the raw gas is not directly correlated to the actual quality of combustion efficiency. It may be concluded again that concentrations of halogenated organic compounds measured downstream of the boiler of an MSWI are the result of "memory effects" integrating the history of the combustion efficiency and fuel composition [12] over many hours before. Real-time data of halogenated organic compounds, such as low chlorinated chlorobenzenes often discussed as surrogates for PCDD/F in the flue gas downstream of a boiler, are not suited as parameters for real-time combustion control of MSWI. They might only be used as a rough indication of enhanced PCDD/F formation in the ash deposits on the boiler surface.

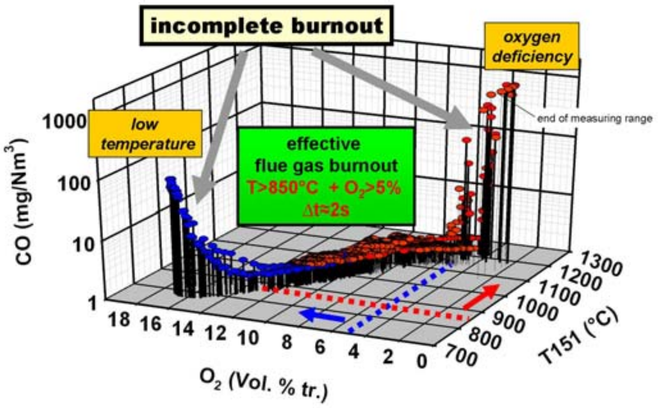

Fig. 4: Characteristics of the flue gas burnout at MSWI.

Of these experimental results, the range of controlled operation of our pilot plant was taken as an example and depicted in Fig. 4. At combustion temperatures (T151) above 850°C, a residence time of >2s inside the flue gas burnout zone, and average concentrations of O_2 >5% in the raw gas, the flue gas burnout was found to be practically completed. Operation outside of this range and in particular under conditions of oxygen depletion should be avoided by all means. Permanently low CO concentrations (indication of low soot formation) and the avoidance of peaks will guarantee low PCDD/F formation.

Locally resolved burnout control of the fuel bed and the flue gas inside the furnace and over the cross section of the post-combustion zone already will contribute essentially to improving the combustion efficiency, the prerequisite of a low overall PCDD/F formation. Today, modern methods are available to monitor the fuel bed burnout by a video and/or IR camera [13] (IR= 3.9µm wavelength). Real-time image analysis [14] provides online information about the combustion situation in the fuel bed over the whole grate area.

The evaluation of the image information from an IR camera by complex mathematical algorithms results in the detection of the location and extension of the major combustion zone as well as in the determination of the temperature distribution of the burning fuel bed over the whole grate area. Local differences in the burnout behavior caused by the inhomogeneous fuel can be recognized accurately and nearly compensated in real time by an automatic control of the primary air supply, grate kinematics, and the waste feeding rate. As a result, a high-quality bottom ash can be achieved. The bottom ash quality can be further improved by operation at long residence time, sufficient oxygen, and high temperatures inside the fuel bed in the last grate zone. Detailed tests at TAMARA with a modified design/operation of the combustion chamber resulted in very low chloride, TOC, and PCDD/F concentrations of the bottom ash (Fig. 5).

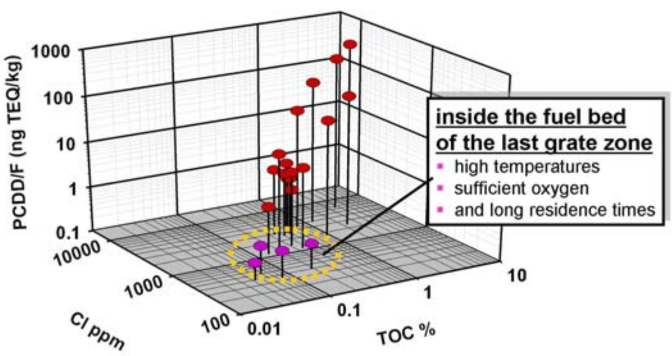

Fig. 5: Improvement of the bottom ash quality.

The dioxin level of the bottom ash under such improved conditions was reduced by about an order of magnitude compared to today's common levels of about 1-5 ng/kg TEQ [15]. This new method will contribute to a further overall reduction of PCDD/F release from MSWI and also support the utilization of the bottom ash as construction material.

Despite an accurate control of the solid fuel bed burnout, the flue gas leaving the fuel bed may vary widely in its local composition (particularly of the heating value) over the grate area with time. The mixing before entering the post-combustion zone is only marginal. The secondary air is usually injected uniformly over the cross section, independently of the actual local need of oxygen and only controlled by the temperature at the end of the post-combustion zone and the average oxygen level in the raw gas downstream of the boiler. As a consequence, small amounts of PICs (CO, C_nH_m, and soot particles) may remain unburned in the flue gas. By using IR and/or video cameras similar to fuel bed monitoring, (observation at defined wavelengths and using modified image processing techniques), the flue gas burnout situation can be characterized over the cross section of the post-combustion chamber in real time. Tests at a full-scale incinerator successfully demonstrated the online detection of sooting areas [16] (strains) fluctuating locally inside the post-combustion chamber. Depending on the local requirements, the secondary air injection can be distributed by individually controlled single air nozzles or by groups of air nozzles. The total amount of secondary air supply will still be controlled by the combustion temperature and the O_2 level in the raw gas.

The question of how efficiently such an optimized distributed secondary air injection improves the flue gas burnout was evaluated in a first step by numerical simulations (FLUENT) for a full-scale geometry using experimental flue gas input data. By comparing common techniques with the new concept of optimized secondary air distribution, it was found that the new sophisticated secondary air injection allows for an operation of MSW incineration plants up to the designed maximum capacity at an almost perfect flue gas burnout over the whole cross section of the flue gas duct preventing PCDD/F formation.

Another experiment revealed that PCDD/F formation under sooting conditions can be inhibited largely by a permanently SO_2-rich operation. It is suggested that the new combustion control technology supports the S recycling process [2] ensuring PCDD/F levels well below the emission limit already in the raw gas even when burning inhomogeneous MSW in full scale.

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