

# DESIGN AND OPERATION OF LOW-PCDD/F MUNICIPAL SOLID WASTE INCINERATION

Hunsinger H, Seifert H, Jay K

Forschungszentrum Karlsruhe GmbH, Institut für Technische Chemie  
D-76021 Karlsruhe, Germany  
[hunsinger@itc-tab.fzk.de](mailto:hunsinger@itc-tab.fzk.de)

## Abstract

Experimental investigations at our pilot incinerator confirmed again that PCDD/F formation by de-novo synthesis<sup>1</sup> from chloride rich fly ash deposits is the dominant formation mechanism.

Increasing only the steam pressure/temperature of the installed boiling water generator at constant combustion conditions showed significantly enhanced PCDD/F formation. This effect was caused by the extension of the de-novo synthesis temperature window over a larger region of the ash covered boiler surface. Operating the steam boiler at the “cold end” at low temperatures leads to rapid cooling down of the flue gas in the most critical temperature range of 450→200°C resulting in low PCDD/F formation.

Sulfation of the fly ash by increasing the SO<sub>2</sub> concentration is known to be effectively reducing the chloride concentration of the fly ash. Thus PCDD/F formation can be inhibited significantly. Evaluation of many experimental data from our plant showed that only moderate SO<sub>2</sub> levels are sufficient for efficient in-flight sulfation of the fly ash before settling down in the critical de-novo temperature region when reducing the cooling down velocity of the hot flue gas in the temperature range of 900→700°C.

Based on these findings low-PCDD/F MSW incineration can be realized by respective modifying the process design and operation.

## Introduction

In MSW incineration 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. By suppressing the formation of pollutants particularly of PCDD/F and NO<sub>x</sub> by economic primary methods, the efforts in flue gas cleaning can be reduced significantly. Such primary measures must act selectively and be in compliance with all other aspects of an optimized waste incineration process<sup>2</sup>.

Incineration of an inhomogeneous MSW causes fluctuating combustion conditions. Despite modern process control technologies MSWI is never 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<sub>n</sub>H<sub>m</sub> and soot particles) leaving the furnace unburned. Time-resolved measurements showed that 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<sup>3,4</sup>. Soot particles, together with chloride-containing fly ashes, are partly separated during heat recovery on the steam boiler surface. In these ash deposits Cl<sub>2</sub> is formed by metal (Cu and Fe-oxides/-chlorides) catalyzed reactions. At temperatures >200°C, PCDD/F formation takes place by oxy-chlorination of the carbonaceous structures (soot) inside the ash deposits. This so-called de-novo synthesis<sup>5,6</sup> is the predominant mechanism for PCDD/F formation of MSW incinerators. The formation reaction is maximized at about 300°C.

One measure minimizing PCDD/F formation additionally to the improvement of the burnout quality of the flue gas particularly of soot is the increase of the SO<sub>2</sub> concentration<sup>7,8</sup>. In a earlier paper<sup>9</sup> we reported that at permanently low HCl/SO<sub>2</sub> ratios (Cl/S ≈ 1-2) in the flue gas during a steadily efficient flue gas burnout (CO ≈ 2mg/Nm<sup>3</sup>, TOC of the fly ash <0.1%), the formation of PCDD/F can be suppressed down to values of <0.1 ng/Nm<sup>3</sup> TEQ in the flue gas upstream of the flue gas cleaning system already. SO<sub>2</sub> levels in the range of 1000mg/Nm<sup>3</sup> were generated in an economic way by a process-integrated SO<sub>2</sub> cycle without any co-combustion

of additional sulfur or sulfur compounds. The high SO<sub>2</sub> concentrations caused a reduction of the chloride content of the fly ash by sulfation reactions resulting in very low Cl<sub>2</sub> formation rates inside the ash deposits on the boiler surface. As a consequence the oxy-chlorination of carbonaceous structures (soot) of the fly ash deposits (de-novo synthesis) is inhibited and results in very low PCDD/F formation rates as well as reduced boiler corrosion rates.

## Experimental

The experimental investigations described below were carried out at our TAMARA pilot plant burning a crushed and homogenized municipal solid waste delivered from a nearby MSW incineration plant. The main data of the furnace are obvious from figure 1. The flue gas is cooled down by passing through a boiling-water steam generator producing saturated steam. The characteristic of this boiler type shows an almost constant temperature of the cooling fluid over the whole steam boiler section over the cooling path of the hot flue gas. The steam pressure can be adjusted in the range of 6 to 30 bar. The removal of the ash deposits from the boiler surface is arranged by a mechanical cleaning device (steel brush) usually operated in 24h intervals. The boiler cleaning efficiency is not complete but sufficient for continuous operation. There are always parts of ash deposits left even after the cleaning procedure. The temperature (T<sub>113</sub>) of the flue gas downstream of the boiler (raw gas) depends on the adjusted steam pressure, the flue gas flow and the fouling situation of the boiler surface. Before entering the flue gas cleaning system the flue gas is further cooled down to ≤200 °C by controlled water injection (quench absorber) in order to avoid PCDD/F formation during dust separation in the fabric filter.

During the investigations the temperatures were monitored at several locations inside of the flue gas ducts. Sampling of PCDD/F and fly ash as well as online monitoring of the flue gas composition (HCl, SO<sub>2</sub>, CO, O<sub>2</sub>, H<sub>2</sub>O etc.) was carried out after the quench adsorber. The experiments lasted over 2 days without changing the combustion conditions. The most important data characterizing the combustion process are summarized in Fig.2. The combustion temperature after secondary air injection (T<sub>151</sub>) ranged around 1000-1050°C at an oxygen level of about 10 Vol. %, dry. CO concentrations were always <3mg/Nm<sup>3</sup>. HCl was found at 600-700 mg/Nm<sup>3</sup> and SO<sub>2</sub> at 300-400mg/Nm<sup>3</sup>.

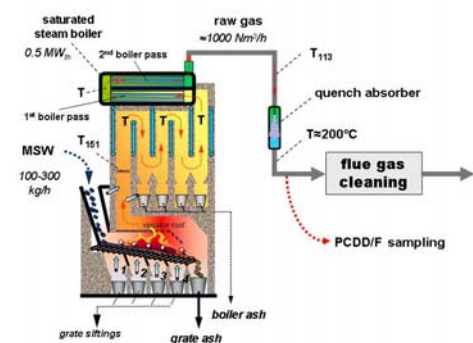


Fig.1: Scheme of the TAMARA pilot MSWI

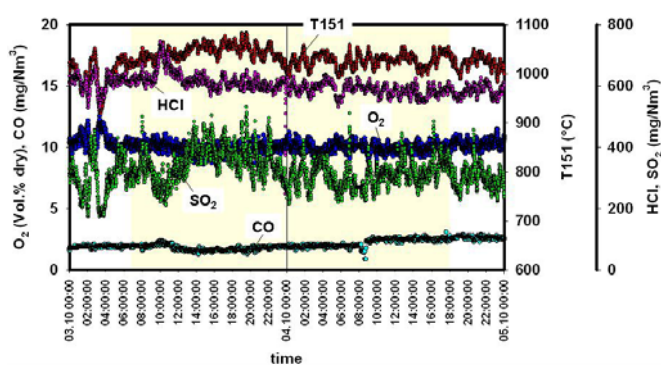


Fig.2: Combustion temperature and raw gas composition

The experimental investigations on PCDD/F formation were started at 7.00 o'clock of the first experimental day by a reference sampling at a steam pressure/temperature of 6bar/180°C. At 10.00 o'clock the steam parameters were increased to approximately 25bar/225°C, kept constant over 24h and subsequently switched back to the starting conditions.

The results of PCDD/F concentrations are shown in Fig. 3. Due to the excellent combustion conditions and the low HCl/SO<sub>2</sub> ratio the PCDD/F concentration of the reference experiment (before steam pressure increase) were found at a rather low level of 0.36 ng/Nm<sup>3</sup> TEQ only. Immediately when increasing the steam parameters pressure/temperature the PCDD/F concentration rose up significantly to concentrations of 6-7 ng/Nm<sup>3</sup> TEQ. During the whole period of elevated steam data the PCDD/F formation remained at these high levels. The ratio

between PCDD and PCDF was almost unchanged while the chlorination pattern of PCDD and PCDF homologues showed a marginal trend to lower chlorination degree during the high boiler pressure phase. The concentrations of chlorinated benzenes and phenol were found to be increased in the same manner as for PCDD/F. Cleaning of the boiler ash deposits obvious from the pressure difference of the flue gas flow (Fig. 4) showed only minor effects on the TEQ concentration. When switching back to initial conditions PCDD/F concentrations dropped down to the same low values as for the starting reference experiment (Fig.3).

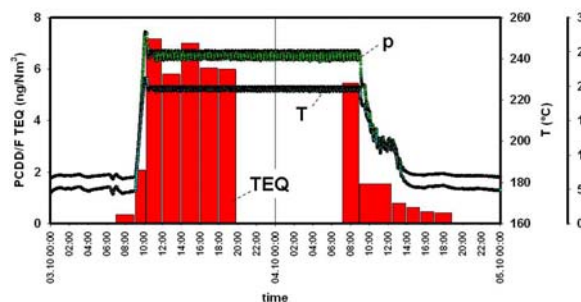


Fig.3: PCDD/F formation during increase of steam parameters (p, T)

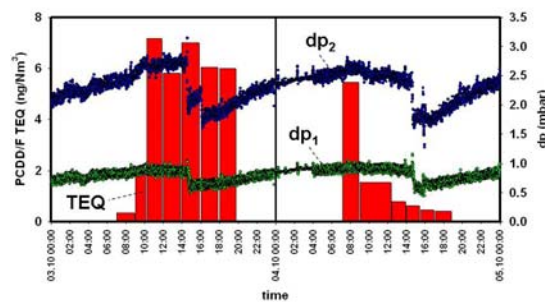


Fig.4: PCDD/F concentrations and deposit cleaning (marked by pressure difference dp)

Increasing the steam pressure/temperature leads to reduced heat transfer from the flue gas to the steam due to the lower temperature difference. Fig. 5a shows the temperature profiles of the flue gas over the heat exchange area of the steam boiler during the experimental duration. As obvious from the graph, the temperature window for PCDD/F formation (200-450°C, maximum at 300°C) is shifted to the boiler end. Cooling down of the flue gas in boiler pass 2 is slower compared to pass 1. In Fig. 5b the ash deposit temperatures at the surface and at the bottom of the ash layer is depicted for boiler pass 1 and 2. The marked temperature range of 300°C represents maximized PCDD/F formation by de-novo synthesis and shows that the boiler area covered with ash within the PCDD/F formation window is extended at the operation with increased boiler pressure/temperature. Additionally the de-novo temperature range stretches out over a much larger part of the thickness of the ash layer (ratio D/d). Taking these considerations into account the total amount of deposited ash within the temperature range of de-novo formation is much higher at higher steam temperatures at the “cold boiler end” compared to the more rapid cooling down situation when operating the boiler with low temperature steam.

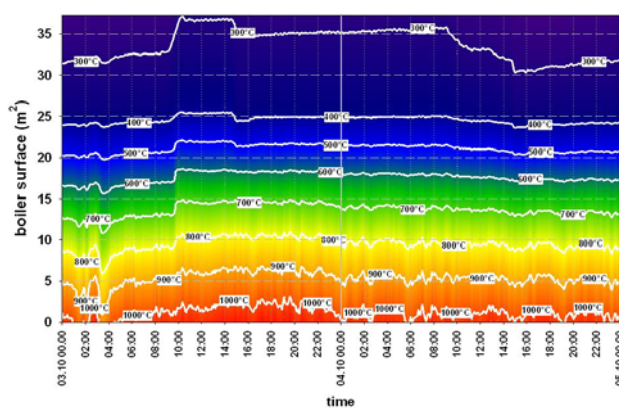


Fig. 5a: Temperature profiles during cooling down of the flue gas in the steam boiler

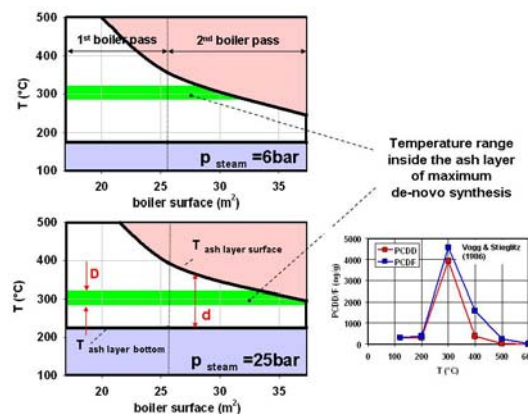


Fig. 5b: Temperature profiles of the ash deposits on the steam boiler surface at the boiler end and locations of maximized PCDD/F formation

The composition of the deposited fly ash varies significantly over the flue gas path in the boiler section. Sampling of the ash deposits from the TAMARA plant and more detailed from a technical MSWI (Fig. 6a, b) reveal that the concentrations of fly ash constituent's (particularly chlorides and Cu) supporting the PCDD/F formation at the “cold end” of the boiler were found to be significantly increased.

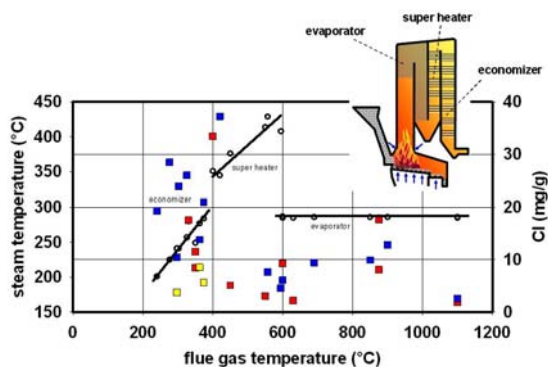


Fig. 6a: Chloride concentration in the ash deposits of a full scale MSWI

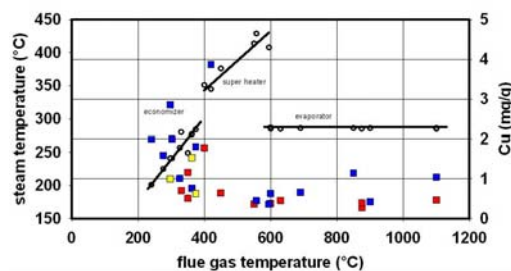


Fig. 6b: Copper concentration in the ash deposits of a full scale MSWI

As described above PCDD/F formation can be inhibited efficiently by sulfation of the fly ash minimizing the chloride concentration. Analytical investigations using X-ray diffraction of fly ash sampled in the raw gas at low and high SO<sub>2</sub> concentrations showed that most of the chloride compounds were almost completely converted to sulfates at high SO<sub>2</sub> levels.

The release of sodium, potassium and metals like copper to the flue gas during solid fuel burnout is favored by the formation of volatile chlorides. NaCl and KCl contribute mostly to the chloride concentration in the fly ash of MSWI. They cause serious corrosion problems as well as PCDD/F formation by forming Cl<sub>2</sub> during reactions with the boiler material (Fe). During flue gas burnout by secondary air injection the alkali chlorides can be converted partly to hydroxides by a temperature depending equilibrium reaction.



During cooling down of the flue gas in the subsequent boiler region the hydroxides can react with HCl or SO<sub>2</sub> forming chlorides and sulfates.



The remaining chlorides can be sulfated by SO<sub>2</sub>.



Sulfation of the chlorides is relatively fast at high temperatures where the chlorides are present in the gas phase. But the reaction is very slow when the chlorides are condensed to the solid phase and deposited on the “cold” boiler surface. Therefore long time is needed to sulfate already existing chloride rich ash deposits necessary to inhibit PCDD/F formation (Fig.7). Reduction of PCDD/F formation will be maximized when sulfation degree of the fly ash is permanently at a high level before entering and settling down in the low temperature region of the boiler.

There are two options to maximize fly ash sulfation efficiency:

- Increasing the SO<sub>2</sub> concentration up to very high levels (Fig.8)
- and/or modification of the process conditions in order to enhance the fly ash sulfation reactions.



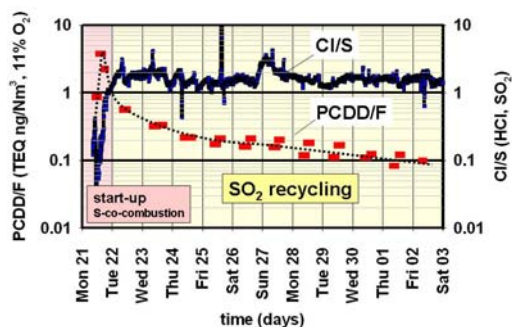


Fig.7: Low PCDD/F formation at permanently high  $\text{SO}_2$  concentrations<sup>9</sup>

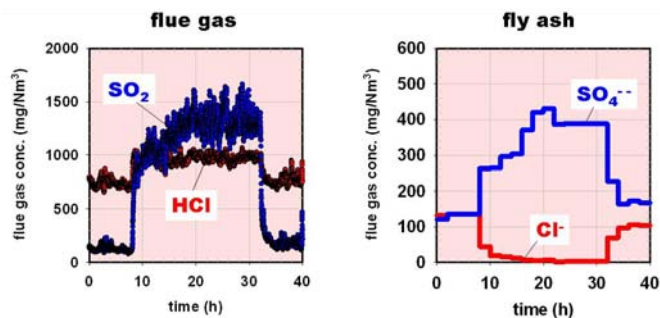


Fig.8: Effect of high  $\text{SO}_2$  concentrations on the Cl and  $\text{SO}_4$  concentration of the fly ash sampled downstream the boiler.

By evaluation of many experimental data from several experimental campaigns at TAMARA burning only MSW, MSWI at elevated  $\text{SO}_2$  concentrations by (a) co-combusting of sulfur, (b) injection of ammonia sulfate in the hot flue gas causing  $\text{SO}_2$  formation by thermal decomposition and (c) recirculation of recovered  $\text{SO}_2$  from the  $\text{SO}_2$  scrubber back to the combustion chamber it was found that the cooling down velocity of the flue gas in the temperature range  $900 \rightarrow 700^\circ\text{C}$  has very significant influence on the fly ash sulfation efficiency. The identified temperature range for fly ash sulfation was confirmed by extra lab-scale experiments. Further detailed investigations revealed that the influence of  $\text{HCl}/\text{SO}_2$  on the Cl/S ratio of the fly ash is significant at the rapid cooling down velocities of  $70\text{-}100^\circ\text{C/s}$  as usually established in commercial MSWI. The influence of the  $\text{SO}_2$  concentration becomes more and more dominant when slowing down the cooling velocity. Fig. 9a shows the experimental data fitted by a linear 2d-correlation of the two most important parameters effecting fly ash sulfation:  $\text{SO}_2$  concentration and cooling down velocity ( $r^2=0.75$ ).

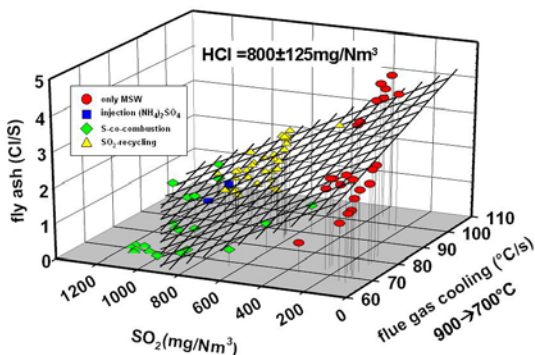


Fig. 9a: Cl/S ratio of the fly ash sampled in the raw gas as function of  $\text{SO}_2$  and cooling down velocity of the flue gas

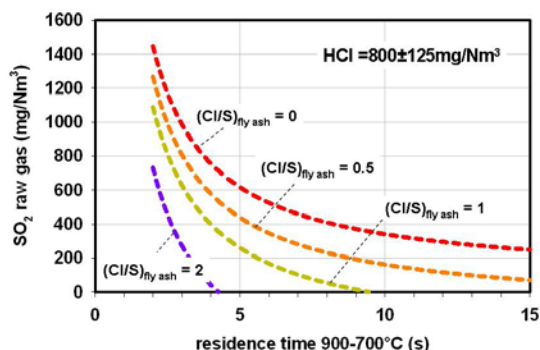


Fig.9b: Needed  $\text{SO}_2$  level for several degrees of fly ash sulfation depending on residence time during flue gas cooling ( $900 \rightarrow 700^\circ\text{C}$ )

Fig.9b shows the results for needed  $\text{SO}_2$  levels in the raw gas for several degrees of in-flight fly ash sulfation depending on the residence time during flue gas cooling down in the temperature range of  $900 \rightarrow 700^\circ\text{C}$ . For low-PCDD/F MSW incineration it can be recommended that modifying the boiler design in order to reduce the cooling down velocity of the flue gas in the high temperature range combined with moderate  $\text{SO}_2$  levels will be the best economic solution.

## Conclusions

De-novo synthesis was identified again to be the main mechanism of PCDD/F formation in MSWI. Low chloride containing fly ash inhibits PCDD/F formation.

From the present findings following conclusions for design and operation of low PCDD/F MSWI can be drawn:

Reduction of the cooling velocity of the hot flue gas in the temperature range of 900→700°C and only moderate SO<sub>2</sub> levels will be sufficient to sulfate the fly ash very efficiently before entering the critical temperature zone of de-novo synthesis. The formed chloride poor fly ash has very low potential for PCDD/F formation.

Increasing the cooling down velocity of the flue gas in the temperature range of 450→200°C reduces additionally PCDD/F formation by minimize the amount of fly ash deposits within the temperature window of de-novo synthesis. Therefore it can be recommended to operate the steam boiler at the “cold end” at low temperatures regarding the acid dew point of the flue gas.

The application of both measures in MSWI design and operation will result in very low PCDD/F formation.

## References

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