

AN ECONOMIC PROCESS TO INHIBIT PCDD/F FORMATION IN MSWI BY SO₂

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Introduction

Municipal solid waste (MSW) is a very inhomogeneous material, which varies widely in its chemical composition and physical properties. Such a difficult fuel is mainly burnt in grate furnaces. Fluctuations of the heating value can widely be compensated by controlling the feed rate, the grate kinematics, and the air supply to guarantee an effective carbon burnout of the bottom ash and of the flue gas. In practice carbon burnout cannot be completed totally. Small amounts of unburnt carbon particles (soot) are always present in the flue gas and cause the formation of halogenated organic compounds like PCDD/F predominantly in the fly ash deposits on the boiler surface at temperatures above 200°C by de-novo synthesis¹.

Apart from the burnout efficiency of the flue gas, PCDD/F formation depends on the chlorine and sulfur concentration of the fuel. Experimental studies by many authors²⁻¹⁰ confirmed a suppressed PCDD/F formation when burning fuels with low Cl/S ratios. In all combustion studies the effect of suppressed PCDD/F formation at increased SO₂ concentrations was explained by the theory of Griffin¹¹, according to which SO₂ reduces Cl₂ and this inhibits the PCDD/F formation.

Own studies¹² on PCDD/F formation depending on the SO₂ level in the flue gas, carried out at our pilot plant TAMARA and at a full scale municipal solid waste incinerator (MSWI), showed no direct correlation. Short term fluctuations of SO₂ had no influence on the formation of PCDD/F and other halogenated organic compounds. Extended time periods up to 40h at high SO₂ levels (incineration of MSW and sulfur) showed only after many hours and after removing the ash deposits from the boiler surface a tendency to decreased PCDD/F formation. These results indicated that only permanently high SO₂ concentrations will be effective in terms of reducing PCDD/F formation. These findings were in agreement with the results of Lindbauer³ who found only after some days significantly reduced PCDD/F formation. This long term effect of inhibited PCDD/F formation by SO₂ reveals that the most relevant mechanism of PCDD/F formation must be attributed to de-novo synthesis of the ash deposits in the boiler. High SO₂ levels in the flue gas cause the sulfation of the fly ashes resulting in very low chlorine content. This leads also to reduced concentrations of CuCl₂ in the fly ashes and avoids the formation of iron chlorides by suppressing the corrosion of the steel surface which takes place below chloride rich ash deposits¹³. Especially these metal chlorides were known to catalyze the formation of Cl₂ inside the ash deposits causing PCDD/F formation^{1, 12, 14-16}.

The in-flight sulfation of vaporized chlorides at high temperature is very fast but reactions with the already deposited chloride rich fly ashes at the boiler surface at low temperatures are very slow. Only after an almost complete sulfation of the boiler deposits the formation rate of PCDD/F will decrease significantly.

Experimental

Combustion processes with effective flue gas burnout and molar Cl/S ratios (HCl/SO₂) of about 1:1 in the raw gas are characterized by very low PCDD/F formation. Therefore it was intended to develop methods to establish permanently increased SO₂ concentrations in an economic way.

The concentrations of total chlorine and sulfur of municipal solid waste in industrialized countries typically range at values of about Cl = 6.9-7.7 g/kg and S = 1-3 g/kg¹⁷. In MSWI only small amounts of sulfur compounds are transferred to the flue gas. Due to the relatively low maximum temperatures inside the fuel bed (<1000°C), sulfur remains in the grate ash mainly in the form of sulfates. As shown in Fig. 1, significant amounts of the S-fraction released into the flue gas are contained in the boiler ashes (mainly CaSO₄).

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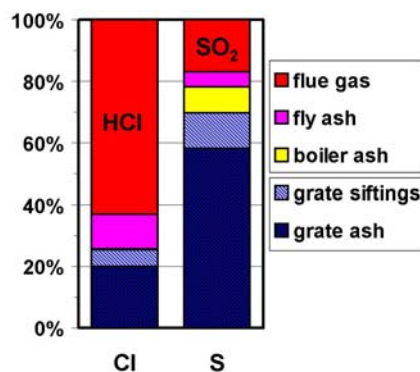
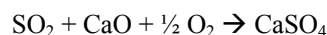


Fig. 1: Partitioning of Cl and S in waste incineration

Heterogeneous reactions of SO₂ and CaO particles in the high-temperature zones of the furnace decrease the SO₂ concentrations in flue gas significantly.



In order to establish high SO₂ concentrations, the release of CaO particles from the fuel bed into the flue gas should be minimized by operating the furnace at a preferably low stoichiometric primary air supply. The lower level of primary air supply is limited by the required amount to complete the carbon burnout of the grate ash.

As shown in Fig. 2 only the reduction of the Ca transfer rates to the flue gas by lowering the primary air supply results in an increase of the SO₂ concentrations from 200 up to about 300 mg/Nm³ while the concentration of HCl is nearly unaffected.

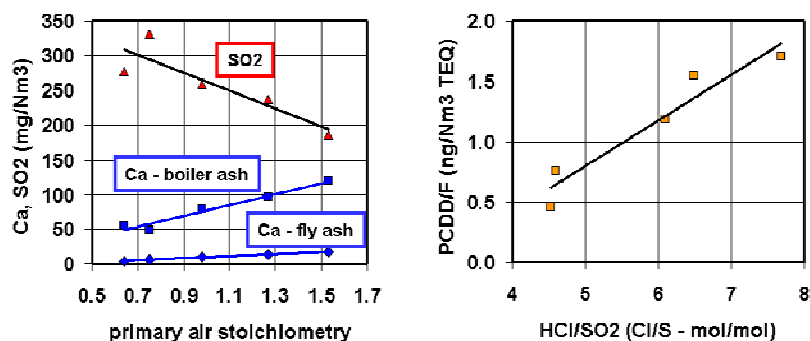


Fig. 2: Increase of the SO₂ concentration by low transfer rates of Ca particles to the flue gas at low primary air ratios and reduced PCDD/F formation at low Cl/S ratios

These small modifications of the furnace operation lead to decreasing Cl/S ratios (HCl/SO₂) in the flue gas and reduced PCDD/F formation. A further increase of the SO₂ concentration by thermal decomposition the highly stable sulfates contained in the grate ash is not possible in technical incineration plants

The generation of permanently high SO₂ concentrations by co-combusting sulfur or sulfur-rich fuels would increase the demand for neutralizing chemicals and cause much higher amounts of residues from the flue gas cleaning devices. These disadvantages would lead to additional costs of thermal waste treatment and counters the benefit of reduced PCDD/F formation.

An economically efficient alternative of establishing low Cl/S ratios in the flue gas is based on the idea of a selective removal of the SO₂ present in the flue gas, followed by recycling parts of the separated SO₂ or S-compounds back to the furnace¹⁸. Such a process causes a SO₂ cycle and leads to elevated SO₂ concentrations between separation unit and re-injection port. The SO₂ concentration established can be controlled by the feed-back rate.

This idea requires a flue gas cleaning system which allows for the selective separation of individual pollutants in defined stages. Especially incinerators equipped with a dust filter (ESP or FF), followed by a two-stage wet scrubbing system (WSS), are well suited for building up such a process-integrated SO₂ cycle.

After dust removal and HCl absorption by water, SO₂ can be separated almost selectively in a second wet scrubber. Various wet chemical absorption processes are available to separate SO₂ from flue gases. The sulfur com-

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pound formed depends on the chemicals added to the scrubbing liquid. If the reaction product shows a low thermal stability, it can be fed back partly directly into the furnace where it is decomposed at the temperatures inside the furnace, thus forming SO₂ again. To realize the idea of a process integrated SO₂ cycle several options are possible. Some examples are described as follows:

1) Sulfuric acid option

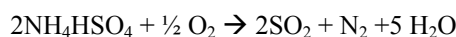
H₂O₂ can be used for separating and oxidizing SO₂ to H₂SO₄. The sulfuric acid can be fed back directly into the furnace where it is decomposed at high temperatures (>900°C), forming SO₂.



In MSWI rather high amounts of H₂O₂ would be needed to reduce the Cl/S ratio significantly. This would be associated with relatively high costs.

2) Ammonia sulfate option

A more economic method might be the use of ammonia as neutralizing agent in the second scrubber to separate SO₂. The formed ammonia sulfate can also be fed back to the furnace where it is decomposed forming SO₂ and partly NH₃.

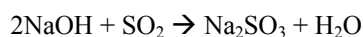


Such a process offers the advantage of a combination of NO_x reduction by SNCR (selective non catalytic reduction) by NH₃ and the inhibition of PCDD/F formation by SO₂.

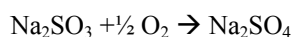
3) SO₂ generation from alkaline sulfites

A third method is the generation of SO₂ from sulfite solutions. The process is as follows:

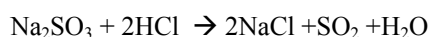
After fly ash separation by an electrostatic precipitator (ESP) or a fabric filter (FF), HCl, HF, and Hg are separated in the first acid scrubber. The acid solution formed of scrubber 1 usually is neutralized after discharge in the waste water treatment process. SO₂ is almost selectively separated in a second scrubber at pH values of ≤7 by the addition of alkaline compounds, for example NaOH.



By modifications of the scrubber parameters (residence time of scrubbing water, pH value ...), oxidation of sodium sulfite to sodium sulfate by O₂



from the flue gas can efficiently be suppressed. Significant amounts of SO₂ can be dissolved additionally in such an alkali sulfite solution. From this sulfite solution, high amounts of SO₂ may be recovered by mixing the acid effluents of the HCl scrubber before neutralization with the sulfite solution of the second scrubber in a small external reactor



The released SO₂ can be stripped by a small amount of inert gas or by flue gas. The SO₂ generated is fed back into the furnace or the hot part of the boiler, preferably into the secondary air. This completes the SO₂ cycle and results in elevated SO₂ concentrations in the flue gas between the furnace and scrubber 2 and in the sulfation of the fly ashes. The principle of the process is summarized in Fig. 3. The maximum amount of SO₂ generated by this process is limited by the amount of HCl available and the sulfite concentration of the SO₂ scrubber. In MSWI the Cl/S molar ratio of the flue gas can be set by this method down to values of about 1:1. The total

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amount of neutralizing agents for the whole wet scrubbing process (scrubbers 1 and 2) as well as the amount of solid residues from flue gas cleaning remain practically unchanged compared to standard operation.

The S-recycle process using the SO₂ generation from a sulfite solution (Fig. 3) was set up and tested for the first time at our pilot plant TAMARA.

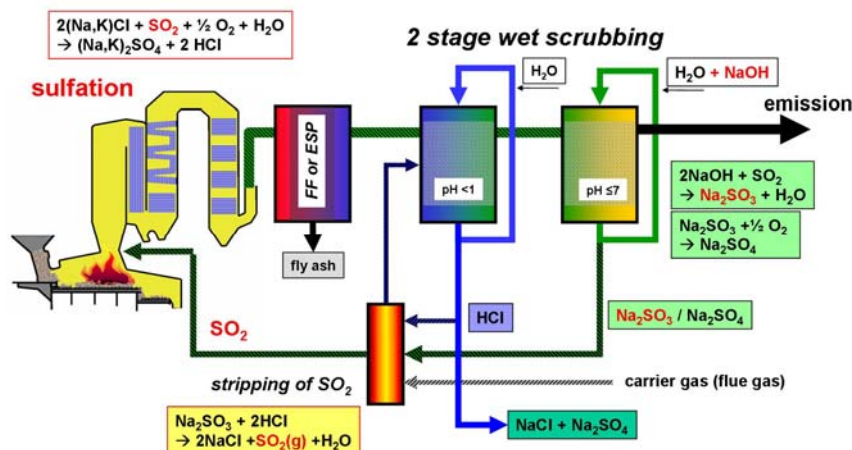


Fig.3: Schematic presentation of the S-recycle process (alkali sulfite option)

Due to the experience of a reduced PCDD/F formation under sulfur-rich start-up conditions¹⁰, the furnace was preheated by the natural gas burner, together with untreated wood chips and SO₂ gas injection. When the temperature of the furnace exceeded 1000°C at the exit of the combustion chamber, the fuel was changed to municipal solid waste. At the same time, SO₂ dosage was switched off and the sulfur recycling process was started.

The furnace was generally operated at low primary air ratios in order to minimize Ca particle transfer to the flue gas and avoid losses of SO₂ by reactions forming CaSO₄.

After start-up of the furnace, the combustion process was run during the first two weeks of the experimental campaign without any disturbances, as is indicated by very low CO data which were constant at values below ≈2 mg/Nm³. The following third week of the campaign was used to investigate effects of defined disturbed combustion conditions. The analytical work is still under evaluation and will not be discussed any further here.

It was possible to establish SO₂ levels up to about 1000 mg/Nm³. Differences of the SO₂ concentration during the experimental time were caused by variations of the operation parameters of both wet scrubbers and the SO₂ reactor in order to optimize SO₂ generation. The HCl data ranged at levels up to about 1000 mg/Nm³.

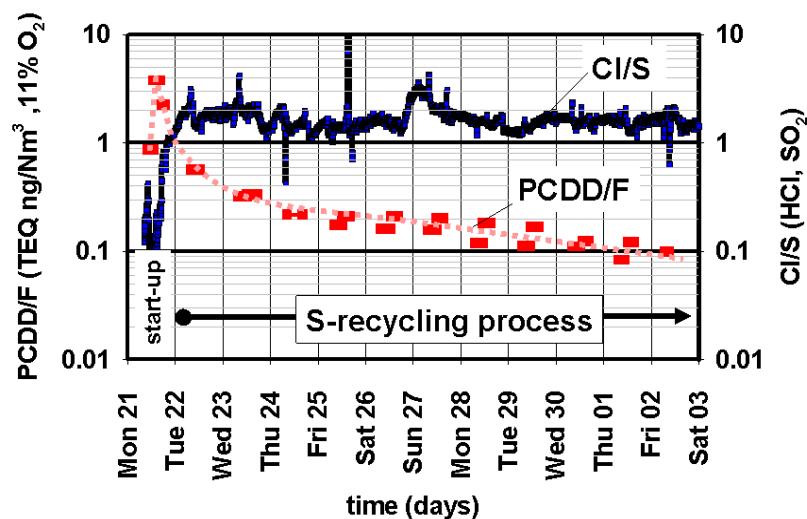


Fig. 4: PCDD/F concentrations in the raw gas

The Cl/S molar ratio (HCl/SO₂) in the flue gas could be lowered to values close to 1:1. The PCDD/F values measured downstream of the boiler in front of the flue gas cleaning system together with the Cl/S ratios (HCl/SO₂) are shown in Fig. 4.

Immediately after completing the start-up procedure of the furnace the PCDD/F concentrations dropped slowly down.

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A few days later, the PCDD/F raw gas data ranged at levels of about $0.1 \text{ ng/Nm}^3 \text{ TEQ}$. Other halogenated compounds like chlorobenzenes and chlorophenoles showed an analogue behavior. This result indicates that the formation of PCDD/F and also other halogenated organic compounds in MSWI could almost be avoided by such a simple and economically efficient primary measure. From these results, it may be concluded that complex flue gas cleaning devices are no longer necessary to meet PCDD/F emission regulations.

The type of the S-recycling process installed had no detectable negative effects on other pollutants especially on the separation efficiency of mercury by the wet scrubbing system. The total Hg concentrations downstream of scrubber 2 were always found to be well below the emission limit of $30 \text{ } \mu\text{g/Nm}^3$.

From the first positive results at our pilot plant TAMARA, it can be concluded that the S-recycling process will contribute essentially to reducing the flue gas cleaning efforts in MSWI.

In wet scrubbing systems (WSS), even at PCDD/F levels below $0.1 \text{ ng/Nm}^3 \text{ TEQ}$, PCDD/Fs are absorbed and enriched up to the absorption/desorption equilibrium in the plastic material depending on the temperature of the scrubber. If the WSS represents the tail end of the flue gas cleaning device just in front of the stack, the PCDD/F absorbed over long terms by the plastic material can be released temporarily during excursions of the scrubber temperatures and lead to elevated PCDD/F concentrations in the stack. To avoid such a “memory effect” in the wet scrubbers, the normally used tower packing of polypropylene (PP) should be replaced by Adiox[®] material¹⁹ (polypropylene matrix in which finely dispersed carbon particles are homogeneously distributed). This material irreversibly absorbs PCDD/F very efficiently also under start-up and unsteady operating conditions. It will act as police filter and result in additional security to always guarantee very low emission values.

Summary and Conclusions

PCDD/F formation in MSWI takes place predominantly by de-novo synthesis from the ash deposits in the boiler. Permanently high SO_2 concentrations cause sulfation of the boiler ash and fly ashes, which leads to low chloride concentrations in the ash deposits. This results in very low PCDD/F formation rates. High SO_2 levels can be established in an economically efficient way by a process-integrated SO_2 cycle only by using the SO_2 present in the process. The process can be supported by reduced transfer rates of CaO particles to the flue gas (to avoid a reduction of the SO_2 concentration by desulfurization reactions) at reduced primary air supply. No additional sulfur dosage is needed. The amount of residues from flue gas cleaning remains constant. No negative effects of the S-recycling process on the separation of other pollutants like Hg could be observed.

The findings of the investigations indicate that the PCDD/F emission standards can be met already upstream of the flue gas cleaning system by primary measures only. The flue gas cleaning efforts can be reduced without changing the emission standards.

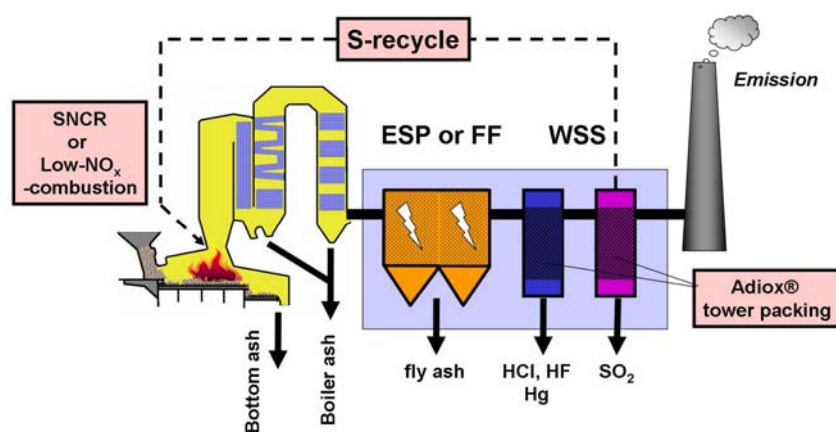


Fig. 5: Concept of optimized MSWI by the implementation of primary measures and reduced flue gas cleaning

The use of the S-recycling process in combination with primary methods for NO_x control (SNCR or low- NO_x combustion²⁰) and the Adiox[®] tower packing in the wet scrubbing system allow for an economically efficient design of the MSWI process, with ecological standards being complied with by a simplified flue gas cleaning system as shown in Fig. 5.

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The next step will be the implementation of the process in a full-scale plant. Major interests will be to demonstrate inhibited PCDD/F formation in practice as well as to investigate how efficiently the boiler corrosion will be reduced under SO₂-rich conditions.

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