PCDD/F-EMISSION CONTROL FOR MSWI BY SO$_3$-ADDITION

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1.   Summary

Follow-up on technical scale (4-6) of theoretical considerations (1-3) of sulphur addition for the sake of PCDDF-control has led to the underlying mechanism of actual reduction of (de-novo) dioxin formation: inhibition by masking of catalytic dust particles by SO$_3$.

It could be shown that only SO$_3$-addition beyond the chemical equilibrium between SO$_3$ and SO$_2$ is the governing parameter. Thus, 150 mg SO$_3$/m³ addition to the raw flue gas has a more beneficial effect for reducing PCDD/F formation than 800 mg/m³ SO$_2$ addition or high sulphur fuel addition (e.g., 1,6 % S coal).

Since the added SO$_3$ adheres to the alkaline filterdust, no increase of SO$_3$ is observed in the clean flue gas after dust control and, consequently, no corrosion induced. Substantial savings may be expected when retrofitting existing plants (with greater 5 ng/m³ PCDD/F emission) with dioxin control measures like catalysts, active coke etc. since SO$_3$-addition limits primary dioxin emission to below 1 ng/m³.

2.   Introduction

Lab tests by Mahle and Whiting 1980[1] have led to theoretical considerations by Griffin 1986[2], patent formulations by Karasek et al. 1988[3], as well as practical data reports that incineration of sulphur containing fuels leads to negligible formation of PCDD/F's.

The underlying theory is given by Griffin's postulation for a low Cl/S-ratio in the gaseouse phase whereby the formation of PCDD/F's and chlorinated aromatics is suppressed by reducing the necessary intermediate Cl$_2$ to HCl by way of

$$SO_2 + Cl_2 + H_2O = SO_3 + 2\,HCl$$
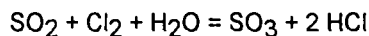
It could be shown in our previous work (4-6), however, that not the Cl/S ratio in the gas phase is the governing parameter as postulated (1,2), but the masking of catalystic dust particle surfaces due to sulphatization with SO$_3$ (not SO$_2$).

3.   Test and Analytical Procedures and Methods

Detailed data, test data, sampling and analyzing procedures are presented elsewhere (Lindbauer et al[4,5,6]). PCDD/F samples of flue gas and filter dust were taken in most test runs at 2 sample points simultaneously: pre- and post-electrostatic precipitator (ESP). The

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analytical methods employed were in agreement with LAGA method 11172, net traverse measurement VDI 2066 followed by separate analyses of the gas and particulate phase with a detection limit depending on phase and homologue state of 0.006 ng/standard cubic meter or better. Further testing and sampling was done also at other ports of various MSWI (municipal solid waste incinerator, furnace chamber, first boiler pass, auxiliary furnace chambers top and bottom) in some cases. The usual plant parameters (boiler data, emission data etc.) were recorded in all cases. Additional measurements were carried out at all PCDD/F sample ports for the following variables: HCl, SO_2, SO_3, NOx, CO, dust, humidity, temperature, O_2, CO_2, in some cases parallel by 2 or even 3 different analytical procedures, especially for SO_3.

4.   Previous Test Programs

The test programs were carried out over a period of approx. 4 years, at different MSWI plant sites, with different sulphur additives and points of admixture. All tests were carried out over longer periods of addition (pre-tests: hours; main tests: week(s); followed or initiated by weeks of regular incineration and a test program for the blank sample value) to reduce memory effects (active catalytic surfaces in dusts administered prior to test additions, lit.4-6).

Coal Tests

Fig. 1

Austrian lignite with a sulphur content of 1,6 % S was added to the waste in the shute at calculated intervals in such manner that a continuously constant SO_2-concentration was achieved throughout all test runs. Pre-tests ("one-day"-addition) overcame the memory effect only at prohibitively high addition of sulphur (up to more than 2000 mg SO_2/m^3), by reducing the TEQ from 8 - 10 ng/m³ to below 1 ng/m³ in the raw gas and from 3 - 8 ng/g filter dust / fly ash to values below 1ng/g (blank test 1 and 7, coal ad- mixtures: test 2 = 30 %, test 3 = 60 %, test 4 and 5 = 20 %).

FIG.1: TE-distribution particulate/gaseous phase
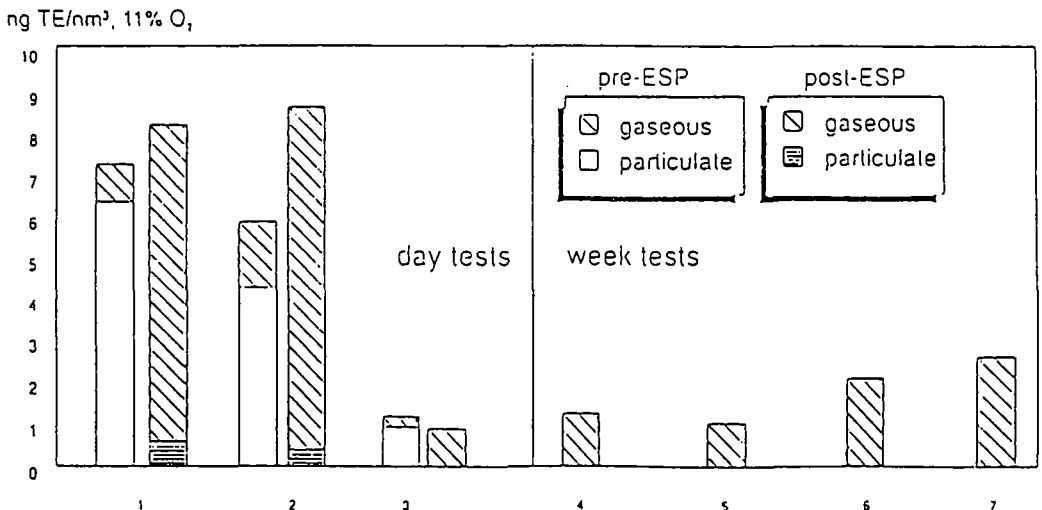pre- and post-ESP

ng TE/nm³, 11% O,

Fig. 1 shows also that there is a distint change of dioxin matrices, across the ESP (electrostatic precipitator): nearly all of the originally de-novo produced dioxin is situated on the dust particles, whereas it is in the gaseous analytical fraction post-ESP where it may perfectly be treated by secondary catalytic means (special denox cat for dioxin control).

5. SO_2 and SO_3-Addition-Tests for inhibition of de-novo Synthesis

Since the addition of S-containing coal or other S-containing waste liquids or solids may not be feasible in many circumstances, another MSWI plant site, and another way of applying sulphur to inhibit PCDD/F synthesis - believed to be only of relevance for the catalytic, heavy - metal containing filter dust particles - was chosen. For a test period of several weeks varying amounts of gaseous SO_3 or SO_2 were added at ports in the economiser section (in a region between 400 and 600°C, i.e. "prior to the de-novo synthesis" near the boiler end section).

The SO_2-concentration (one-week-test) was chosen in the order of the 20%-coal addition test 4 and 5 of Fig. 2 carried out before, i.e. at around 700 mg SO_2/m^3 to compare effectiveness of the addition method (e). The SO_3-addition was carried out over several weeks at a much lower concentration in the off- gas from the furnace chamber and varied from 50 to 150 mg/m³ addition-concentration (b-d). No SO_3-increase was found down-stream from the addition port.
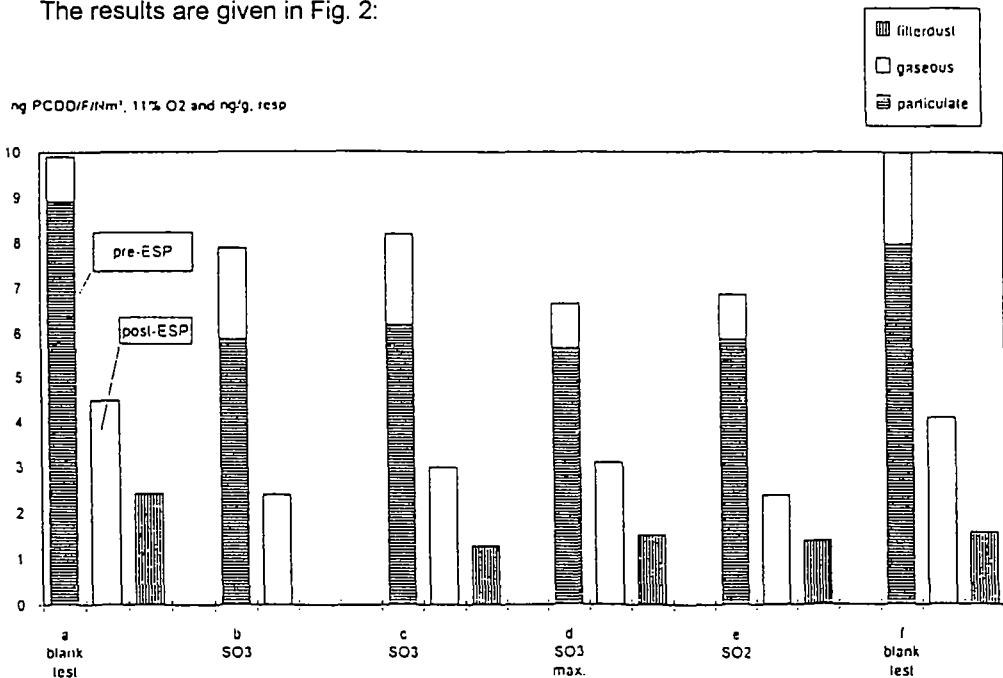
The results are given in Fig. 2:

FIG.2: TE-values pre-/post-ESP and filter dust

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The most striking effect, however, can be taken from the fact that no reduction to below 3-5 ng TEQ/m³ in the gas and to below approx. 1.5 ng TEQ/g in the filter dust occured, invariable with the length of the addition of either SO_3 or SO_2, at whatever concentration. Further measurements determined the reason for this: this plant had a low temperature zone right past the furnace chamber (for other design reasons) which initiated de-novo synthesis before the first boiler pass with TEQ values of 10 ng/m³ and more contrary to usually very low values in this region. Conclusion: already synthesized PCDD/F's are "not inhibited" by addition of either SO_2 or SO_3.

6.   New tests with SO_3
At yet another MSWI plant SO_3-tests (addition 150 mg SO_3/m³) have been carried out meanwhile. Very low values of TEQ, indeed, have been reached proving the correctness of our conclusions and the effectiveness of SO_3 for inhibiting PCDD/F's; detailed data are presented in fig. 3 and table 1 resp.

Whereas the SO_3-addition test, was carried out in a "clean boiler" for one full week (right after start-up after the annual re-vamping) the blank tests (weeks later) again show the continuing increase of TEQ in gas and filter dusts, resp. measurement data in the shaded boxes give values obtained from discontinous measurements (average over the PCDD/F Sampling period of approx. 8 hours), all other data originate from continous monitoring apparatus during the same period, except "SO_2 + SO_3" which was done by wet discontinuous analysis in adjacent measuring ports during the same test period (mean values).

7. DISCUSSION AND OUTLOOK
There seems to be sufficient evidence now that by addition of SO3 only substantial reduction from originally high TEQ-values of up to approx 15 ng/m³ to values below 1 ng TEQ/m³ may safely be reached, with no increased SO_3-levels in comparison to regular SO_3-concentrations (cf. Table 1: SO_3/pre- and post-ESP).
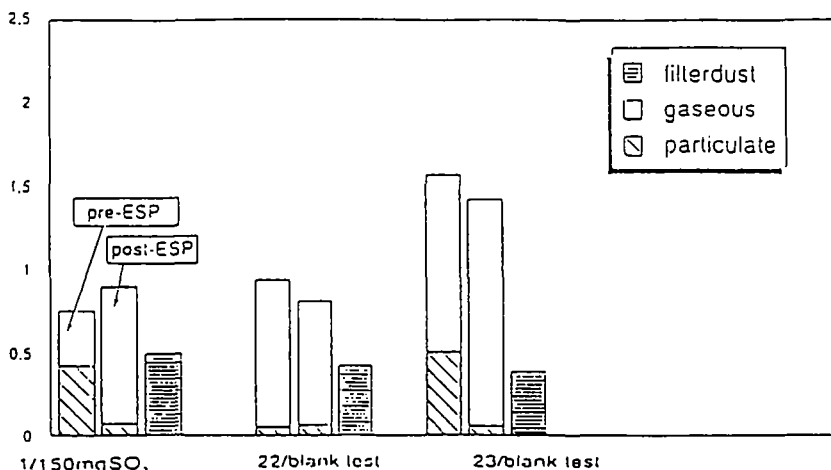
FIG.3. TE-values pre/post-ESP and filter dust   SO₃ Tests

Table 1: SO3-Tests (11%O2, dry)

PARAMETERS	1/150 mg SO3/Nm³			22/BLANK TEST			23/BLANK TEST			UNIT
	pre-ESP	post-ESP	FA	pre-ESP	post-ESP	FA	pre-ESP	post-ESP	FA	
O2	10.1	10.0		9.5	9.5		8.7	8.6		%
CO2		9.1			9.3			10.7		%
SO2		336			256			321		mg/Nm³
SO2 + SO3	410	299		478	397		261	219		mg/Nm³
CO		22			20			21		mg/Nm³
TOC		1.9			4.0			3.3		mg/Nm³
Temp.	162	159		166	163		163	159		°C
dust	648	6		739	3		614	1		mg/Nm³
H2O	80	82		86	86		95	97		g/Nm³
HCL	568	452		432	386		464	300		mg/Nm³
SO3	40	10		33	43		45	29		ng/Nm³
TEQ gas	0.29	0.83		0.87	0.75		1.13	1.39		ng/Nm³
TEQ part	0.41	0.03		0.02	0.03		0.43	0.03		ng/Nm³
TEQ sum	0.70	0.85		0.89	0.77		1.56	1.42		ng/Nm³
TEQ FD			0.5			0.40			0.71	ng/g
NOx		691			655			717		

For retrofits to existing plants the application of this process may be of interest for the reduction of TEQ to below 1 ng/m³ (substantial savings and safer lay-out of dioxin-reduction catalysts) as well as the reduction of TEQ dust concentrations in the boilers themselves (labor hygienics considerations).

References:
1 Mahle, N., Whiting, L: Chemosphere 9, 693, 1980
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