## PCCD/F EMISSION CONTROL BY SULPHUR ADDITION - NEW RESULTS WITH HIGH - S LIGNITE, $SO_2$ AND $SO_3$

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### 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 by Hagenmaier 1989[4] 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

$$SO_2 + Cl_2 + H_2O = SO_3 + 2\ HCl$$

Due to the fact that at least 10 chemical - in combination with several physical and instrumental-parameters (cf. a detailed description by the authors elsewhere[5]) cloud the issue of a complete understanding of PCDD/F-formation and destruction from the furnace grate via boiler section, gas cleaning plant to the stack, it is of no great surprise that results so far published seem inconclusive. All reports published so far BMFT/UBA/ARGUS[6], Düwel[7], Johnke[8], Vogg et al[9] show no substantial reduction of PCDD/F's, especially in the dusts themselves. Rather short test periods and sulphur addition intervals chosen as indicated in all other reports except ours (Lindbauer et al[10]) makes one draw the conclusion of having observed "memory effects" (Vogg et al[9]) induced by heterogeneous PCDD/F-formation from dust layers from furnace chamber till stack of municipal solid waste incineration (MSWI) facilities.

### Test and Analytical Procedures and Methods

Detailed data, test data, sampling and analyzing procedures are presented elsewhere (Lindbauer et al[5]). 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 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 (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 $SO_3$.

## $SO_3$- and $SO_2$-Addition

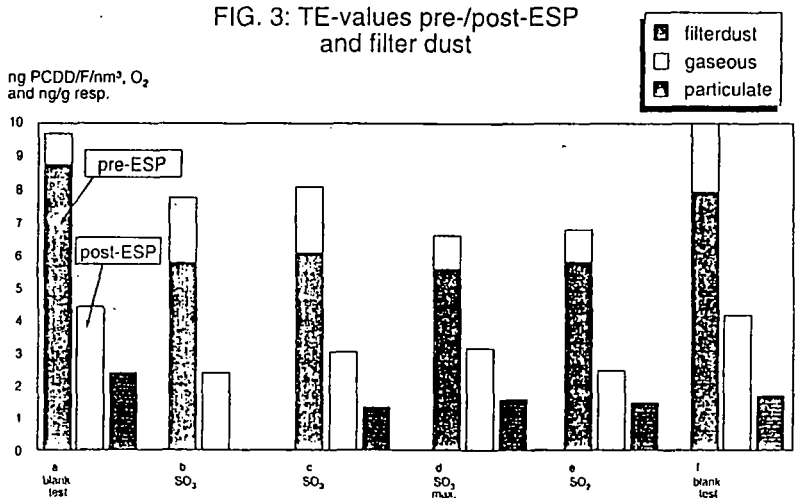
The addition of S-containing coal or other S-containing waste liquids or solids may not be feasible in many circumstances. Therefore, to increase the credibility of the theory another way of addition, another MSWI plant site, and another way of applying sulphur to inhibit PCDD/F synthesis - believed 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 $SO_3$ 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 $mg/m^3$ addition-concentration (b-d). No $SO_3$-increase was found down-stream from the addition port. $SO_3$-measurements were carried out with 3 different sets of apparatus and methods during the tests continuously and simultaneously: pre-ESP, post-ESP.

Blank tests (a and f) show the expected high raw-gas concentration of PCDD/F as TEQ's pre- and post-ESP/particulate and gaseous phase as well as the filter dust value ng TEQ/g. Since the total dust concentration in this new plant was much lower than in the coal test plant, a significantly lower dust concentration was present in the clean gas (post-ESP), i.e. also a reduction effect of the total TEQ from pre-to post-ESP (approx. "50 %") can be seen.

The results are given in Fig. 3:

FIG. 3: TE-values pre-/post-ESP and filter dust



## Test Program

The test program was carried out over a period of approx. 3 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).

## Coal Tests

Fig. 1 and Fig. 2
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 admixtures: test 2 = 30 %, test 3 = 60 %, test 4 and 5 = 20 %).

FIG. 1: TE-values pre-/post-ESP and filter dust

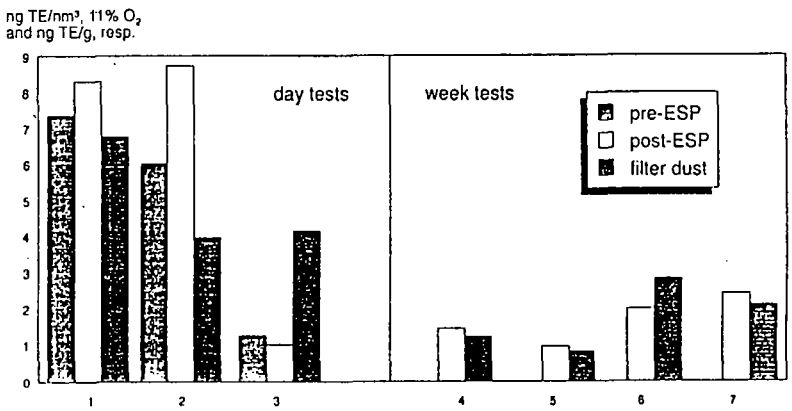
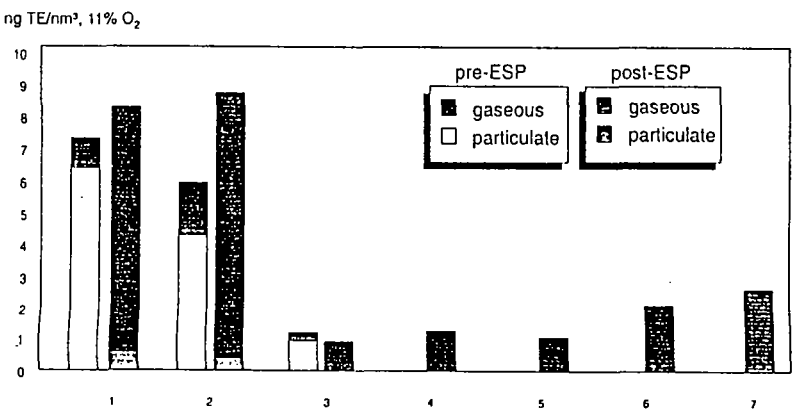



FIG. 2: TE-distribution particulate/gaseous phase pre- and post-ESP



## De-Novo-Synthesis and Inhibition Effect

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. It rather shows that the lower level stays "frozen", invariable with the length of the addition of be it $SO_3$ 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 leads to a mixture of cold and hot gas and dust streams thereby initiating de-novo synthesis before the first boiler pass with TEQ values of 10 ng/m³ and more whereas in usual plants only values around the detection limit and lower are reported in this region. Conclusion: Already synthesized PCDD/F's are not inhibited by addition of $SO_2$ or $SO_3$.

## New tests with $SO_3$

At yet another MSWI plant $SO_3$-tests have been carried out meanwhile. Very low values, indeed, have been reached proving the correctness of our conclusions and the effectiveness of $SO_3$ for inhibiting PCDD/F's; detailed data will be presented.

Literature:
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