# INHIBITION OF PCDD/Fs FORMATION BY THIOUREA

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## Introduction

China urgently requires much more modern municipal solid waste (MSW) disposal capacity. Yet, despite increasingly stringent national standards for PCDD/Fs emissions, there is still strong opposition against any PCDD/Fs emissions from such sources. Chemical suppression is a promising preventive technique, since several compounds containing S or N show sizeable suppression of PCDD/Fs formation. Compounds containing both S and N should be the most effective, due to their distinct inhibition mechanism [1-3]. Based on this hypothesis three compounds with high and combined S/N-content were selected and tested, including $(NH_4)_2S_2O_3$ (ANT, ammonium thiosulfate), $(NH_2)$-$SO_2$-$(OH)$ (ASA, aminosulfonic acid) and $CS(NH_2)_2$ (TUA, thiourea). This paper shows results from three test series conducted with TUA, with S (N) content (wt. %) of 42% (37%).

## Materials and methods

A synthetic model fly ash (MFA) was composed of (in wt. %) 91.8% of $SiO_2$, 3% of activated carbon, 5% of NaCl and 0.2% of $CuCl_2$, corresponding to an elemental fly ash load of ca. 3.1% Cl, 0.1% Cu, and 3% C. In each test run the amount of MFA was 2g, whether with suppressant added, or not (reference test).

The laboratory scale test facility (Fig.1) comprises a tubular reactor and furnace, with three sections of 0.5 m, featuring independent heaters and temperature controllers to maintain the desired temperature profile. The external and internal diameter of the quartz reactor tube is 45 mm and 30 mm, respectively. The inhibitors tested are well mixed with MFA (except for test M) and located between two silica wool layers in the internal tube. The simulated flue gas (300 ml/min; 12% vol. $O_2$ in $N_2$) flows through the MFA; experimental test conditions are listed in Table 1. Three test series I, II, III, were conducted to vary the molar ratio (S+N)/Cl, the reaction temperature and the addition methods, respectively. In test G, the exhaust stream was monitored by means of a Gasmet unit. The analysis of PCDD/Fs samples was conducted according to USEPA method 1613. The results are based on all isomer groups TCDD to OCDF and on the seventeen toxic 2,3,7,8-substituted PCDD/Fs,

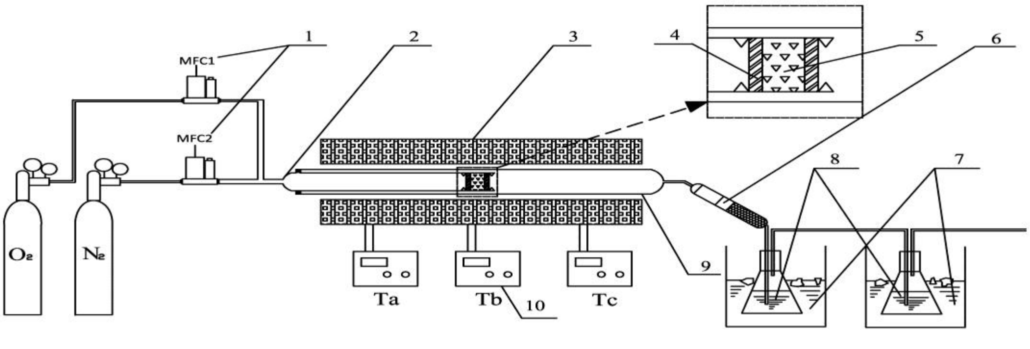

Figure 1. Scheme of the reactor facility.
1-mass flow meter; 2-inner tube; 3-tube furnace; 4-silica wool; 5-model fly ash; 6-XAD - II resin; 7-ice bath; 8-toluene; 9-outer tube;10-temperature controller;11-water-bath kettle.

Table 1. Experimental design.

| Exp. No. | Inhibitor TUA | T, °C | (S+N)/Cl | Test series | Exp. No. | Inhibitor TUA | T, °C | (S+N)/Cl | Test series |
|---|---|---|---|---|---|---|---|---|---|
| F-1 | none | 350 | 0 | I,II,III | T | 0.06 g | 650 | 1.4 | II |
| F-2 | none | 650 | 0 | II | M [a] | 0.06 g | 350 | 1.4 | III |
| A-1 | 0.02 g | 350 | 0.47 | I,II,III | G-1[b] | none | 350 | 0 | III |
| A-2 | 0.06 g | 350 | 1.4 | I | G-2[b] | 0.06 g | 350 | 1.4 | III |
| A-3 | 0.10 g | 350 | 2.34 | I | | | | | |

Notes: The conditions of the PCDD/Fs formation tests (F) and the inhibition tests (A, T, M, G) were: 50 min, 12 vol. % $O_2$ in $N_2$ [a]. Instead of mixing with MFA, in test M the TUA was placed in front of MFA and separated from it by the silica wool layer, and this was the only difference between test I-2 and M. [b] The reaction conditions of test G-1 and G-2 were all the same as those of test F-1 and A-2, respectively, but the exhaust stream was monitored by the Gasmet monitor and the PCDD/Fs formed was not analyzed.

## Results and discussion

The suppression result on PCDD/Fs is shown in Table 2, for various conditions of TUA-addition. In test series I, this inhibition ratio of both PCDD/Fs formation (ng/g) and international toxic equivalent quality (I-TEQ/g) exceeded 97%, despite a low (0.47) molar ratio of (S+N)/Cl. As more TUA was added (3%, 5%) suppression of both PCDD/Fs and I-TEQ was almost 100%. Therefore, a higher molar ratio (S+N)/Cl led to more effective suppression, at least within a certain range.

The ratio of PCDDs/PCDFs declined after TUA addition, indicating stronger suppression of PCDDs than of PCDFs. On the whole, the weight averaged chlorination degree of PCDD/Fs lessened with rising TUA addition, indicating a negative effect of TUA on chlorination. The fingerprint of the seventeen 2,3,7,8-substituted PCDD/Fs showed (Fig. 2) that OCDD, 1,2,3,4,6,7,8-HpCDF and OCDF were the major congeners. Still, 2,3,4,7,8-PeCDF contributed most to the I-TEQ value, due to the toxic equivalence factors (TEF), followed by 1,2,3,4,6,7,8-HpCDF. In the homologue distribution of PCDD/Fs (Fig. 3) addition of TUA led an increasing proportion of low chlorinated PCDDs, like T4CDDs and P5CDDs, and this explains the chlorination degree reduction. For PCDFs, this phenomenon was different and this revealed the dissimilar formation and inhibition mechanism of PCDDs and PCDFs.

<Table 2> Results regarding the inhibition effects of TUA under various conditions

| Items | F-1 | A-1 | A-2 | A-3 | F-2 | T | M | Units |
|---|---|---|---|---|---|---|---|---|
| PCDDs | 761±94 | 10±10 | 0.285±0.009 | 0.36±0.19 | 0.466±0.097 | 0.179±0.027 | 209±102 | ng PCDD/g MFA |
| PCDFs | 1773±175 | 54±43 | 4.34±0.32 | 4.2±2.05 | 0.745±0.098 | 0.315±0.0048 | 605±194 | ng PCDF/g MFA |
| PCDDs/PCDFs | 43±6 | 19±6 | 6.6±0.3 | 8.5±0.3 | 62.6±4.8 | 56.7±2.6 | 34.5±6.1 | %, PCDDs/PCDFs |
| ΣPCDD/Fs | 2534±222 | 65±53 | 4.6±0.3 | 4.6±2.2 | 1.2±0.2 | 0.49±0.03 | 814±296 | ng PCDD-F/g MFA |
| I-TEQ | 77.7±33 | 0.92±0.7 | 0.095±0.019 | 1.02±0.08 | 0.034±0.015 | 0.018±0.0029 | 5.1±1.4 | ng I-TEQ/g MFA |
| PCDD/Fs inhibition, % | 0 | 97.5±2.1 | 99.82±0.01 | 99.83±0.09 | 0 | 59.2±2.6 | 69±12 | %, PCDD/Fs |
| I-TEQ inhibition, % | 0 | 98.8±0.9 | 99.88±0.03 | 99.87±0.1 | 0 | 48±8.6 | 93.4±1.8 | %, I-TEQ |
| Cl-PCDDs | 7.54±0.09 | 7.65±0.24 | 6.21±0.32 | 6.20±0.36 | 6.45±0.05 | 5.94±0.009 | 7.84±0.01 | Weight average level of chlorination. |
| Cl-PCDFs | 6.61±0.01 | 6.96±0.17 | 6.86±0.06 | 6.67±0.14 | 6.45±0.03 | 6.20±0.008 | 7.22±0.04 | |
| Cl-PCDD/Fs | 6.77±0.09 | 7.03±0.19 | 6.86±0.08 | 6.63±0.16 | 6.45±0.01 | 6.12±0.011 | 7.34±0.05 | |

Notes: series I included the tests labeled F-1, A-1, A-2, A-3; series II included the tests labeled F-1, A-1, F-2, T; series III included the tests labeled F-1, A-1, M.

In series II (at 650 °C, instead of 350 °C) the amount of PCDD/Fs (1.2 ng/g.) formed (F-2) was about three orders of magnitude lower than that for reference test (F-1). Compared with F-1, a reduction of chlorination degree and of the fraction of highly-chlorinated PCDD/Fs could be observed in F-2, following enhanced de-chlorination at higher temperature. A further decrease of both was clearly observed after adding TUA (T). Hence, the inhibition on I-TEQ was only ca. 48%, much lower than that of PCDD/Fs (ca. 60%). Moreover, at 650°C (F-2, T) the major contributor to the I-TEQ value turned out to be 2,3,7,8-T4CDD and 1,2,3,7,8-P5CDD, with a total contribution of 40-50%. All these indicate that formation and its suppression strongly depend on reaction temperature. The lower inhibition efficiencies of both PCDD/Fs and I-TEQ provides scientific basis for selecting the injection point of TUA in a full-scale incinerator. The recommended temperature would be around 350 °C.

Suppression of PCDD/Fs and I-TEQ might be due to thermal decomposition products of TUA. The tests in series III aimed at exploring this possibility. Yet, suppression was much lower than in test A-2, with an efficiency of only 69%. The proportion of highly-chlorinated PCDD/Fs (especially OCDD/OCDF) increased obviously. Due to the higher average chlorination degree, the inhibition efficiency of I-TEQ reached as high as 93%, much higher than the corresponding value based on PCDD/Fs concentration. The total OCDD and OCDF fraction reached ca. 76%, that of 1,2,3,4,6,7,8-HpCDF 19.1%.

Based on the results and those from test A-2, it was supposed that the inhibitory gases decomposed by TUA only played a minor role in PCDD/Fs suppression.

The exhaust stream (analyzed in test G-1 and G-2) is shown in figure 4. Without TUA addition (figure 4a; G-1), the only gas detected was CO and this gas was exhausted after about 30 min, indicating the time length of carbon oxidation and PCDD/Fs formation in our test. The addition of TUA led to completely different emission gases. Decomposition of TUA led to the release of $SO_2$, $NH_3$, known as inhibitory gases. The amount of $SO_2$ discharged was substantial, yielding a potential explanation of the suppression by the S- in TUA. Although Gasmet tests could only provide qualitative perception, it actually also did show a small amount of $NH_3$ released. The inhibition efficiency in test M was not as high as that in test A-2. All the results above led us to come to the conclusion that N- in TUA might play a role in inhibiting PCDD/F formation mainly in the form of $–NH_2$. Primary amines ($-NH_2$) in TUA might be converted into copper nitride, and thus deactivate the catalyst by formation of nitride layers blocking active [4].

## Conclusions

In this work three suppressants combining S and N in their basic molecule were tested and in this paper the results are presented for the most powerful of the three, thiourea (TUA). The results were compared for the reference case (350 °C; no TUA addition) and with suppression. Already at low dosage TUA is shown to be a very powerful suppressant; the results and fingerprints are compared at three addition levels.

In order to establish optimum conditions suppression is tested at 650 °C. Its efficiency is much lower, yet the PCDD/F generation in a reference experiment is already three orders of magnitude lower.

Finally, two modes of application (admixing, upstream thermal decomposition are compared). The first is obviously superior.

This exploratory research thus selected the best performing out of 3 suppressants combining S and N in their molecule. An effective dosage was established for thiourea, as well as a provisional optimum temperature. Some suppression is caused by thermal decomposition, yet the admixing with the model fly ash is the best method of application.

## Acknowledgements

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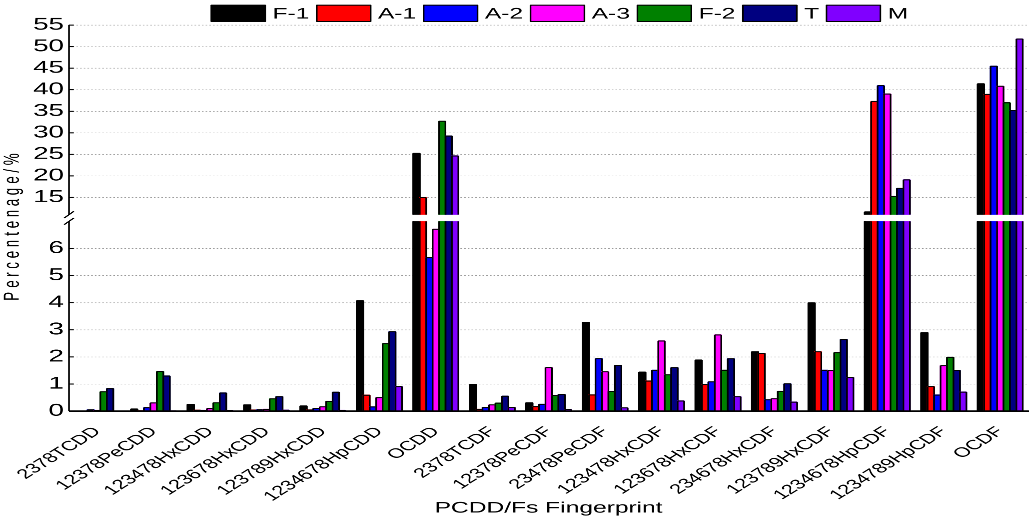

**Figure 2.** The fingerprint of the seventeen toxic 2,3,7,8-subsstituted PCDD/Fs.

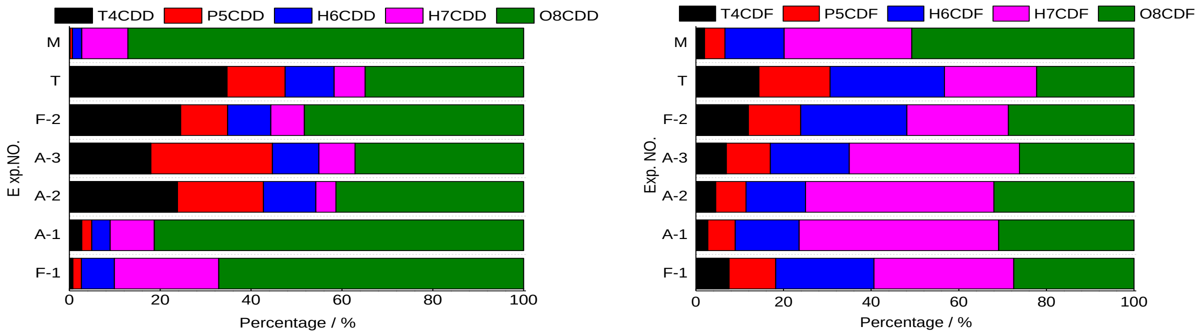

**Figure 3.** The homologue distribution of all PCDD/F-congeners (P = 4 to 8).

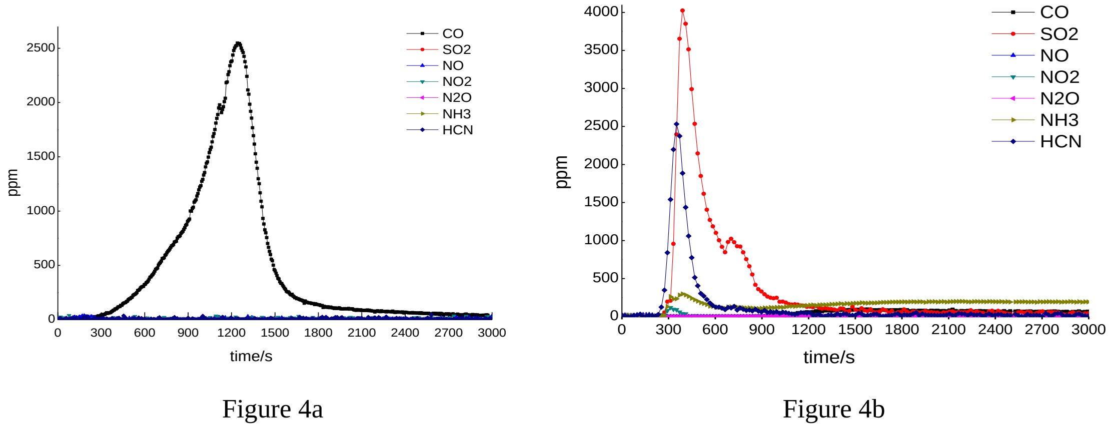

Figure 4a

Figure 4b

**Figure 4.** Emission of common gaseous pollutants during experiments G-1 (without any inhibitor) and G-2 (with addition of 3% TUA).