

## EQUILIBRIUM CALCULATIONS FOR BETTER UNDERSTANDING OF THE EFFECTS OF SO<sub>2</sub> AND H<sub>2</sub>O<sub>2</sub> ON THE DE NOVO SYNTHESIS OF PCDD/F IN THE N<sub>2</sub> + 10% O<sub>2</sub> ATMOSPHERE UNDER MODEL LABORATORY CONDITIONS

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### Introduction

A decrease in the formation of PCDD and PCDF by de novo synthetic reactions in the presence of SO<sub>2</sub> has been demonstrated in many technological applications, especially during combustion and co-combustion of sulfur-containing coal. However, the mechanism of the SO<sub>2</sub> effect on de novo synthetic reactions has not yet been unambiguously explained and some controversial findings reported in the literature have not yet been clarified.

Lee et al.<sup>1</sup> have shown that SO<sub>2</sub> inhibits the formation of PCDD more easily than that of PCDF. Stieglitz et al.<sup>2</sup> have demonstrated on a model fly ash in a humid atmosphere (100 g H<sub>2</sub>O/m<sup>3</sup>) and in the presence of SO<sub>2</sub> (300 mg/m<sup>3</sup>) at 300 °C that the production of PCDD and PCDF by de novo synthetic reactions actually increased by 17 and 49%, respectively. A decrease in the formation of PCDD/Fs under the influence of the same concentration of SO<sub>2</sub> has, however, been found for a Mg-Al-silicate matrix.

A high efficiency in destroying PCDD and PCDF is exhibited by hydrogen peroxide<sup>3</sup>, even at very low concentrations (100 mg H<sub>2</sub>O<sub>2</sub>/m<sup>3</sup>). Preliminary results on the effect of water, hydrogen peroxide, sulfuric acid and sulfur dioxide on a 100 kW circulating fluidized bed combustor have been published by Punčochář et al.<sup>4</sup>.

The present work aims at verifying the effects of SO<sub>2</sub> and hydrogen peroxide on the formation of PCDD and PCDF in a laboratory model system consisting of fly ash from municipal waste incinerator (soxhlet-extracted with toluene), CuCl<sub>2</sub>·2H<sub>2</sub>O, NaCl and activated carbon at a temperature of 300 °C in the atmosphere of N<sub>2</sub> + 10 vol.% O<sub>2</sub>.

### Experimental

The well homogenised mixture of fly ash (0.44 g), NaCl (0.428 mmol), CuCl<sub>2</sub>·2H<sub>2</sub>O (0.064 mmol) and of carbon (1.998 mmol) was placed at the bottom of a U-shaped glass tube. In experiments with anhydrous CuSO<sub>4</sub> (0.073 mmol), the conditions were identical with those for CuCl<sub>2</sub>·2H<sub>2</sub>O. The flow rates of N<sub>2</sub>+10% O<sub>2</sub> and of SO<sub>2</sub> were 10 ml/min. Prior to experiments, the systems were thoroughly washed with the above gases for 15 min. These gases were passed through water at laboratory temperature, then preheated at ca 300 °C and introduced into the reaction system, which was heated to 340 °C for one hour. Unheated hydrogen peroxide (6%) was added to the dry preheated gases at the inlet to the U-shaped reaction vessel at a rate of 0.1 mmol/min.

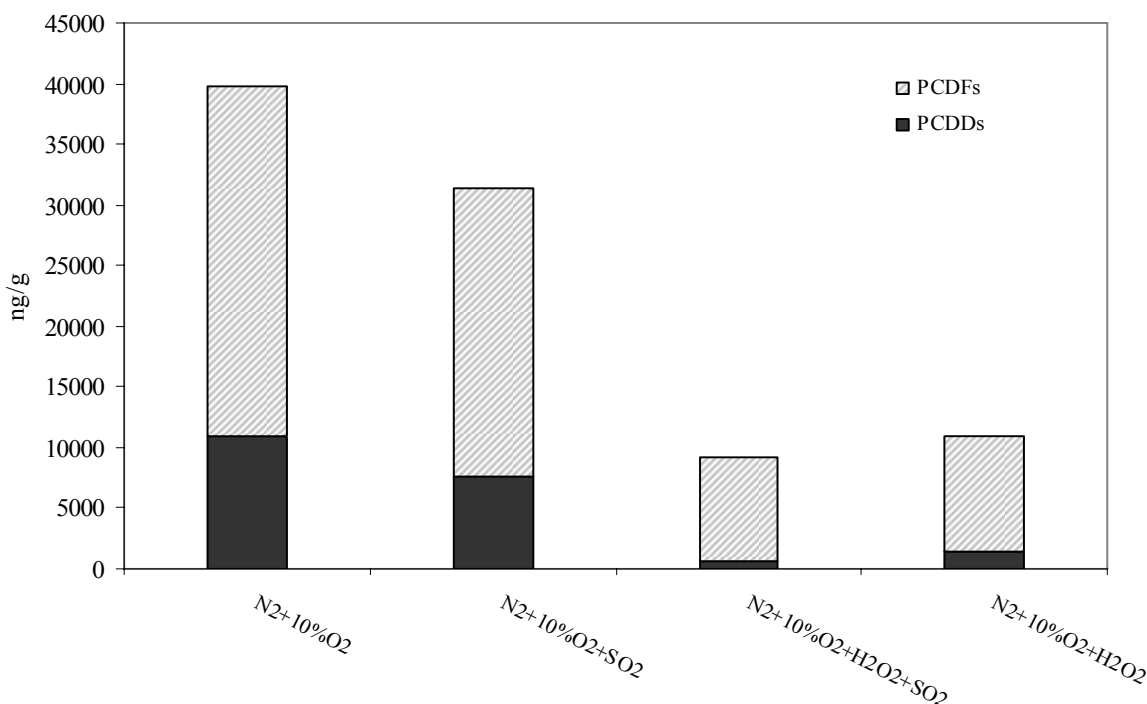
### Results and discussion

#### *The effect of sulfur dioxide and hydrogen peroxide on PCDD/F formation*

The influence of sulfur dioxide on de novo synthetic reactions producing PCDD and PCDF in the N<sub>2</sub> + 10% O<sub>2</sub> system can be seen in Fig. 1. It has been found that the inhibiting effect of SO<sub>2</sub> is substantially more pronounced for PCDD than for PCDF (a decrease by 31 and 17%, respectively). The effect of SO<sub>2</sub> led to a decrease in the total toxicity by 35% for PCDD and by 20% for PCDF. An addition of H<sub>2</sub>O<sub>2</sub> to the original system that only contained 10% O<sub>2</sub> in a nitrogen atmosphere caused a decrease in the PCDD and PCDF production by 87 and 67%, respectively. The PCDF : PCDD ratio increased 2.6times compared to the system not containing hydrogen peroxide, from 2.62 to 6.83, which unambiguously indicated significant destruction of PCDD. If both hydrogen peroxide and SO<sub>2</sub> were added to the system, the decrease in the formation of dioxins and dibenzofurans were

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even higher by 94 and 71%, respectively. The PCDF : PCDD ratio almost doubled, from 6.83 to 12.3, which indicates that a mixture of hydrogen peroxide with sulphur dioxide primarily destroys PCDD.



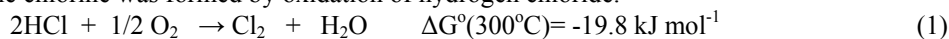
**Figure 1.** Effect of oxygen, hydrogen peroxide and sulphur dioxide on the PCDD and PCDF formation

### *Equilibrium calculations*

The experiments lasting mere one hour might be considerably removed from the equilibrium state. Nevertheless, we calculated the chemical equilibrium for the given experimental conditions in order to obtain more information on the studied system, considering these reaction input components: oxygen, water vapour, SO<sub>2</sub> as the flow-through gaseous phase, and finally sodium chloride and cupric chloride dihydrate; the water liberated by dehydration of CuCl<sub>2</sub>·2 H<sub>2</sub>O was also considered. Furthermore, the reaction products were also included into the calculations, namely, the gaseous SO<sub>3</sub>, HCl, chlorine, CuCl and Cu<sub>3</sub>Cl<sub>3</sub>, and the solid components, CuO, CuSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>. The calculations were carried out by minimizing the total Gibbs energy of the system, while observing the mass balance for all the components present at a temperature of 300 °C and the atmospheric pressure. As gas-solid equilibria were always involved, the calculations always assumed that the least stable solid phase (here CuCl<sub>2</sub>) was present at least in a minimum amount at equilibrium. Equilibrium concentrations of HCl, Cl<sub>2</sub> and O<sub>2</sub> in the studied systems were calculated.

### *Discussion*

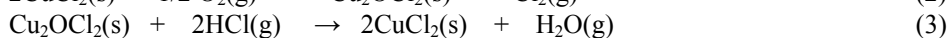
Highly chlorinated PCDD/F was formed in all the studied systems. The chlorination by chlorine might occur when the chlorine was formed by oxidation of hydrogen chloride.



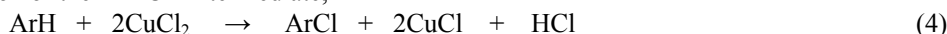
$\Delta G^\circ$  value was calculated by using the data of Chase<sup>5</sup>. According to Ruokojärvi et al.<sup>6</sup>, this so called Deacon reaction is thermodynamically preferred within a temperature range of 250 – 600 °C. However, also the formation of copper(II) oxychloride complex intermediate is supposed. Geiger et al.<sup>7</sup> have described a catalytic effect of cupric chloride in the oxidation of hydrogen chloride by cupric oxide that has been formed by the oxidation of CuCl<sub>2</sub> by oxygen at temperatures of 250 - 400 °C. Cupric chloride has been denoted as the Deacon

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reaction catalyst. The mechanism was described in further works<sup>8,9</sup> where an intermediate of cupric oxychloride,  $\text{Cu}_2\text{OCl}_2$  ( $\text{CuO}\cdot\text{CuCl}_2$ ), is considered as a catalytic component of the hydrogen chloride oxidation according to the reactions,

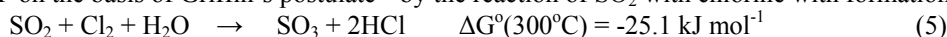


However, cupric chloride may also initiate chlorination processes at aromatic nuclei on the principle of copper-catalyzed single-electron reaction (Nonhebel<sup>10</sup>; Weber et al<sup>11</sup>), when the following reaction takes place with the formation of the  $\text{ArHCl}^\cdot$  intermediate,

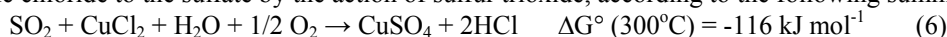


We have calculated that the equilibrium concentrations of HCl,  $\text{Cl}_2$  and  $\text{O}_2$  for the system  $\text{N}_2 + \text{O}_2$  correspond to 0.48, 0.55 and 8.83 mol.%, respectively.

In the systems where sulfur dioxide is present, the equilibrium concentrations of HCl are very high (ca. 68-69 % mole), whereas chlorine and oxygen are almost absent. Lindbauer et al.<sup>12</sup> explain the decrease in the formation of PCDD/F on the basis of Griffin's postulate<sup>13</sup> by the reaction of  $\text{SO}_2$  with chlorine with formation of  $\text{SO}_3$ :



The  $\text{SO}_3$  formed is supposed to be the inhibitor of the PCDD/F formation. Deacon reaction (reaction 1) generating chlorine from hydrogen chloride is opposed to the Griffin postulate (reaction 5). The high equilibrium concentrations of hydrogen chloride and low concentrations of chlorine and oxygen in systems where  $\text{SO}_2$  is present lead us to the assumption that the opposing reactions 1 and 5 do not predominate in the studied system. It follows for equilibrium in the  $\text{N}_2 + \text{O}_2$  system with sulfur dioxide that the conversion of sulfur dioxide to the trioxide is to about 90% complete. Therefore, we assume that high HCl concentrations stem from the conversion of cupric chloride to the sulfate by the action of sulfur trioxide, according to the following summary reaction,



which confirms its thermodynamic feasibility and a considerable probability of its occurrence. Similar conversion of  $\text{CuO}$  by sulfur oxides with formation of  $\text{CuSO}_4$  was presented by Gullett et al<sup>14</sup> and Tuppurainen<sup>15</sup>. Therefore, we experimentally checked the decrease in the production of PCDD/Fs due to the formation of cupric sulfate (Table 1.). It is further known that chlorides of copper are converted into the sulfate in the presence of sulfur within a temperature range of ca 100 – 500 °C<sup>16</sup>. Moreover, the sulfate is thermodynamically much more stable, as compared with cupric chloride. It is evident from our results that de novo syntheses are virtually absent when using cupric sulfate in the reaction system because the PCDD/Fs concentrations are more than three orders of magnitude lower than those with cupric chloride. The results unambiguously verify the fact that the reactivity of cupric chloride, from the point of view of de novo synthetic reactions, is several orders of magnitude higher than that of  $\text{CuSO}_4$ .

**Table 1.** De novo synthesis of PCDD and PCDF in the system  $\text{N}_2+10\% \text{O}_2$  for copper chloride and sulfate (ng/g)

	$\text{CuCl}_2$	$\text{CuSO}_4$
PCDDs	11000	3.94
PCDFs	28800	22.6
PCDD/Fs	39800	26.5

As emphasized above, hydrogen peroxide destroys PCDD much more than PCDF. However, hydrogen peroxide is a strong oxidant and the oxidative destructions of the dioxin and furan oxygen rings cannot at present be elucidated. The calculations of the equilibrium concentrations have shown that the chlorine concentration is relatively high (0.48 mol.%), compared to the preceding experiments, however, it is comparable with the  $\text{N}_2 + \text{O}_2$  system (0.55 mol.%). The equilibrium concentrations for HCl and  $\text{O}_2$  correspond to 0.96 and 6.92 mol.%, in a good agreement with values of 0.48 and 8.83 mol.% for the  $\text{N}_2 + \text{O}_2$  system. The lower concentrations of HCl and higher concentrations of  $\text{Cl}_2$  might result from the catalysed Deacon reaction which is more effective under highly oxidizing conditions.

### Conclusions

From the equilibrium calculations it seems highly probable that the presence of cupric chloride in the system is the main reason for the formation of the highly chlorinated compounds by Nonhebel copper-catalysed single electron reactions (reaction 4). However, under the given experimental conditions, the cupric chloride can also enable the catalyzed Deacon reaction (reactions 2 and 3) and direct oxidative conversion of cupric chloride to the sulfate.

### Acknowledgements

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