### Dioxin '97, Indianapolis, Indiana, USA

### Preliminary Investigation of Formation Mechanism of Chlorinated Dioxins and Furans in Industrial and Metallurgical Processes

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### Introduction

The past years have seen an active research into the mechanism of dioxin formation in combustion processes related particularly to municipal and hazardous waste incineration and other waste processing operations. Processing and recycling of waste materials are practiced in a number of industrial and metallurgical processes such as iron ore sintering and copper smelting plants, and chlorinated organic compounds are sometimes introduced into the processes as plastics-containing steel and copper scraps are used as feedstocks. These chlorinated organic compounds may increase dioxin formation in these operations, and since the flue gas flow volume discharged from these installations is very large, the problem of dioxin pollution by industrial processes deserves attention.

In the international research literature there are only a few study reports concerning this. The report by Riss<sup>1</sup> gave the PCDD/F measurements in a copper reclamation plant. Before plant modification, the PCDD/F emissions were as high as 46-155 ng-TE/Nm<sup>3</sup>; after plant modification, the PCDD/F emissions were drastically reduced to below 0.9 ng-TE/Nm<sup>3</sup>. Laue et al.<sup>2)</sup> have reported that the dust from flue gas cleaning devices in an aluminum recycling plant contains about 40 µg/kg total PCDD/Fs. Lahi<sup>3</sup> has reported that the PCDD/F concentration of clean gases discharged from sintering plants of steel industry is in the range of 3-10 ng-TE/Nm<sup>3</sup>. Another study by Jager<sup>4)</sup> has shown that in steel reclamation plants the raw gas PCDD/F levels are about 1.7 ng-TE/Nm<sup>3</sup>, while the clean gas are 0.04 ng-TE/Nm<sup>3</sup>. These data indicate that flue gas and dust from industrial processes sometimes have PCDD/F concentrations comaprable with that from waste incinerators.

Regarding the formation mechanism of PCDD/Fs in industrial and metallurgical processes little work has been done before. The tests cited above are generally not detailed enough for mechanism elucidation or parameter study. A recent test at a copper smelting plant in Germany has provided more data. The general observation is that the PCDD/F concentration at smelting furnace outlet is extremely high due to the reducing or pyrolytic

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conditions in the fumace; these PCDD/Fs can be effectively destroyed using a postcombustion chamber. However, after the postcombustion chamber PCDD/Fs are regenerated in the boiler section by a factor of about 10 for PCDD and 80 for PCDF. A portion of the PCDD/Fs in the flue gas are then collected by the bag filter. From this observation we suppose that similar to waste incinerators, PCDD/F are formed in the low-temperature region of the copper smelting plant through the *de novo* synthesis reaction or aromatic compounds condensation both catalyzed by copper in fly ash. A study of the fly ash metal composition and morphology and the *de novo* synthesis potential from industrial processes should therefore be useful for eludjation of the PCDD/F formation mechanisms, which is essential for development of practical control measures.

### Experimental

Fly ash samples were taken from the hoppers of waste heat boiler, plate cooler, and bag filter of a copper smelting plant. Scanning electron microscopy (SEM) is utilized for observation of the fly ash morphology, elemental analysis and particle size estimation. Thermogravimetric analysis (TGA) is used to estimate the free moisture content, the loss of hydrate water, the presence of carbon, and the evolution of volatile salts and/or decomposition of salts, carbonates and sulphates. The TGA was done in a helium and a helium/oxygen atmosphere. For the purpose of testing the *de novo* synthesis potential, some sample of fly ashes are subjected to thermal treatment at 300°C for 2 hours in air, and PCDD/F analyses are performed for the original and annealed fly ashes, using the experimental setup and procedure at FZ Karlsruhe as described previously<sup>5</sup>.

#### Results and discussion

Zinc and lead are the most abundant elements in all samples (Zn: 35-45% wt, Pb: 20-30% wt). The concentration of zinc increases with the pathlength of the gasflow starting from the furnace. The concentration of lead on the other hand decreases. Copper is present in a lower extent (2.5-3.5% wt). Other elements include O, Cl, Si, Ca, K. Under SEM examination the boiler ash is seen to consist of small crystallites (size 1-10  $\mu$ m) which coagulate to spherical structures with a diameter between 20 and 120  $\mu$ m. Needle structures (probably ZnCl<sub>2</sub>) are observed (length 1-2  $\mu$ m). The cooler ash has a very irregular structure. It consists of very small crystallites (ZnCl<sub>2</sub> crystals) are observed. The filter dust consists of very fine crystallites (size: 0.25-1  $\mu$ m). They coagulate mainly to spherical structures having a diameter between 10 and 200  $\mu$ m. A few spherical crystals (diameter approximately 20  $\mu$ m) are observed.

The results of TGA for the boiler ash are shown in the figures. The first phenomenon in a  $He/O_2$  atmosphere is a very slight gain in weight which occurs possibly owing to adsorption of oxygen, or oxidation of metals and formation of higher oxides. Drying occurs at a maximum rate at the temperature of 66°C in He and 73°C in  $He/O_2$  resulting in a weight loss of 0.83% and 0.25% respectively. A major weight loss of 2.2% at 183°C under He and 1.7% at 191°C under  $He/O_2$  is observed which is probably due to the occurrence of

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dehydration of "hydrates". Zinc hydroxide is known to decompose at 125°C, lead hydroxide at 145°C. As for drying there is a marked endothermic effect during dehydration. Carbon oxidation is not seen as there is very little if any oxidation phenomenon taking place between 250 and 375°C. There is no identification of an exothermic peak in this temperature range. It is concluded that carbon-in-fly ash is below detection limits, estimated at most 0.1-0.2%. A major peak occurs with weight loss of 15.8% at 683°C under He and 13.2% at 698°C under He/O<sub>2</sub> because of the volatilation or decomposition of the metal compounds. Several supplemental peaks are also present. For the cooler and filter ash the main features of TGA are similar to the boiler ash. The weight loss is always higher under reducing conditions than under oxidizing ones.

The *de novo* synthesis potential of the fly ash samples is tested by thermal treatment of the sample at 300°C for 2 hours in air. For the boiler ash, the total amount of PCDD is increased by a factor of 1.8 and PCDF by a factor of 2.5 in the thermal treatment. PCPh and PCBz are increased by a factor of 27 and 43 respectively. However, for the cooler and filter ash the amount of PCDD and PCDF are decreased after the treatment although PCPh and PCBz are still increased. Thus it seems that the *de novo* synthesis potential of the boiler ash from the copper smelter is rather weak and the cooler and filter ash have no *de novo* synthesis. This could be due to the extremely low carbon content in the fly ashes as carbon in fly ash is generally believed to be the carbon source for the *de novo* synthesis.

These results show that PCDD/F formation in the copper smelter is partly due to the *de novo* synthesis occurring on fly ashes. But the low-temperature formation of PCDD by a factor of 10 and PCDF by a factor of 80 in the real plant has not been fully explained by the laboratory experiments. Then the condensation of precursor compounds may be a more important pathway of PCDD/F formation than *de novo* synthesis for this plant, or maybe there are other unkown mechanisms of PCDD/F formation in industrial installations due to the different fuels and processes involved. It has been shown in previous experiments<sup>6</sup> that addition of the salts of  $Zn^{2^+}$  and  $Pb^{2^+}$  to fly ash model mixtures results in a minor production of PCDD/F. For the case of fly ashes from copper smelting plant the elements Zn and Pb are abundant, so that these elements may play a role in catalyzing the *de novo* synthesis of PCDD/F.

To our knowledge, apart from the above copper smelter data there are only two published data sets for industrial processes showing the low-temperature postcombustion formation of PCDD/Fs. One is that by Laue et al.<sup>2)</sup> for an aluminum recycling plant where the dusts collected at the furnace (800°C position) have total PCDD/F concentration in the order of 1  $\mu$ g/kg; the dusts in the channel (400°C) have about 8  $\mu$ g/kg; and the dusts from flue gas cleaning device (100-200°C) have about 40  $\mu$ g/kg. Another is by Taucher et al.<sup>7)</sup> for a waste oil furnace where the PCDD/F concentration at furnace outlet is about 1.5 ng/m<sup>3</sup>, but rises to 11.5 ng/m<sup>3</sup> at the stack. On the basis of these data one may speculate that PCDD/F formation in the low-temperature postcombustion zone is a common phenomenon for many types of thermal processes. Also, a number of reasons<sup>80</sup> such as the similar dioxin fingerprints from all combustion sources suggest that the dioxin formation mechanisms in all combustion processes are similar, and the *de novo* synthesis from carbon in fly ash is

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likely to be one of these common mechanisms. Further experimental work is much needed to study these observations.

#### Conclusion

The dioxin concentrations of flue gases from some industrial and metallurgical processes such as copper and steel making processes sometimes are comparable with those from waste incinerators according to previous reports. Since the flue gas flow volume from industrial installations is very large, this problem of dioxin pollution deserves attention. Very little is known about the mechanism of dioxin formation in these industrial processes. In this preliminary work, fly ash samples have been taken from a copper smelting plant, and charaterized for chemical composition and morphology and tested for the *de novo* synthesis potential. It is shown that PCDD/F are formed on the boiler ash when subjected to thermal treatment at 300°C for 2 hours in air, but PCDD/F are not formed on the cooler and filter ashes. It is suggested that in the actual copper smelting plant some PCDD/Fs formed in the low-temperature postcombustion zone is from the *de novo* synthesis occurring on the boiler ashes. More experimental work is required to fully elucidate the mechanism and obtain quantitative information about the control parameters in order to facilitate the development of practical control measures.

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