

Laboratory Studies on the Formation of PCDD/F in Secondary Aluminium Processes

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Introduction

Aluminium recycling processes are sources of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF). PCDD/F are supposed to result mainly from organic impurities attached to the aluminium. For the development of minimisation strategies it is important to investigate the mechanisms of PCDD/F formation. The laboratory experiments reported in this contribution were designed to simulate the conditions of large scale-plants and a pilot scale-furnace, operated by the VAW aluminium AG. These investigations are part of a project jointly performed by the Technical University of Munich, the GSF – National Research Center for Environment and Health, and the VAW aluminium AG (Department of Research and Development), which focuses on the technical aspects of the melting process. Combustion studies in the laboratory at 800 °C with used beverage cans (UBC) as aluminium scrap with attached organic material and melting salt showed the potential for PCDD/F formation. UBC is not typical for a large-scale plant but are available in relatively homogeneous composition. Furthermore, UBC were assumed to produce high PCDD/F emissions due to their high organic carbon content so that effective PCDD/F minimisation can more easily be identified in the pilot-scale plant.

The mechanisms of PCDD/F formation in the postcombustion zone were examined for the aluminium recycling process in experiments with fly ash from different sampling points of the pilot-scale plant. Two surface-catalysed reactions were investigated: de novo synthesis from added carbon and synthesis from pentachlorophenol as a precursor. These reactions have been proven to be most relevant in waste incineration but their relative importance is still under discussion [1, 2].

Materials and Methods

Original fly ash (2 g) from the pilot-scale plant was treated in a quartz tube which was inserted in a laboratory furnace. The fly ash was heated to 300 °C and flushed with synthetic air at a flow rate of 50 ml/min. The reaction times were 10 min and 2 h. For de novo

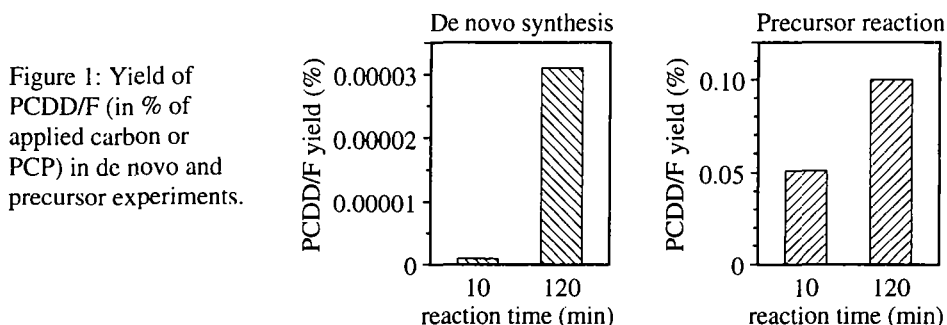
experiments 2 % activated carbon were mixed with the fly ash. In the precursor experiments 100 µg $^{13}\text{C}_6$ -pentachlorophenol (PCP) was added to a quartz wool plug at the top of the fly ash bed. The reaction products were trapped in an ice-cooled impinger filled with toluene. Prior to analysis, the fly ash was treated with diluted HCl, dried and extracted for 24 h with toluene. The extract and the toluene from the impinger were combined.

Aluminium scrap and melting salt were treated in a Bayer-ICI-Shell-furnace (reaction parameters in Table 1), which was heated to 800 °C and moved over the sample. The reaction products were trapped in toluene and analysed.

Seventeen $^{13}\text{C}_{12}$ -2,3,7,8-PCDD/F congeners were used as internal standards, except for the precursor experiments in which $^{37}\text{Cl}_4$ -2,3,7,8-TCDD was added prior to extraction. The clean-up was carried out with chromatographic columns (a column with activated silica and silica coated with sulfuric acid, a column with basic activated alumina). $^{13}\text{C}_{12}$ -1,2,3,4-TCDD was added as recovery standard. The identification and quantification were performed with high resolution gas chromatography and mass spectrometry [3].

Results and Discussion

The low concentrations of PCDD/F (2 ng 1-TE/kg) and organic carbon (0.1%) of the two original fly ash samples from the pilot-scale plant did not require a pretreatment before the de novo and precursor experiments performed for 2 h at 300 °C. In preliminary experiments no PCDD/F were formed with original fly ash. Elementary carbon was added to the fly ash because soot formation was observed during discontinuous feeding of Al scrap into the pilot-scale rotary furnace. The yield of $^{13}\text{C}_{12}$ -PCDD/F from $^{13}\text{C}_6$ -PCP after 10 min was in the same order of magnitude compared to the 2 h experiment. Contrary, the yield of PCDD/F from carbon in the de novo experiments increased substantially with reaction time (Figure 1). The PCDD/F formation resulted from a surface-catalysed process on the fly ash, which contained copper in the mg/kg range and iron in the g/kg range.



In addition, the de novo and precursor experiments (2 h) were performed with a second fly ash. A correlation between metal content and PCDD/F formation was not obvious, but will be further investigated with other fly ash samples. The copper and iron contents of the fly ash were in the same range as for the other fly ash sample, but the PCDD/F formation from activated carbon was about a factor of 20 lower, while the formation from PCP was in the same order of magnitude.

For PCDD/F reduction, it is necessary to improve the combustion of the organic material and to avoid deposition of fly ash in the postcombustion zone. Besides, the incomplete combustion followed by PCDD/F formation could be a reason for PCDD/F formation in the pilot-scale plant even if no organic material is fed into the furnace. This is typically be considered a memory effect.

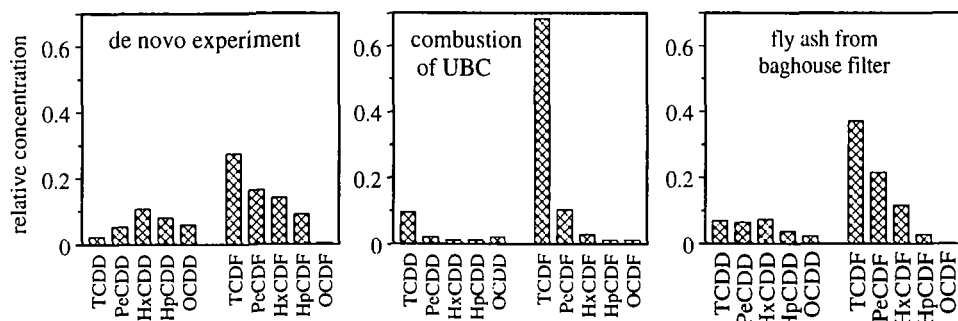


Figure 2: Homologue patterns of PCDD/F from a de novo experiment (2 h), a laboratory combustion of UBC (15 min) and a fly ash from the pilot-scale plant.

The PCDD/F formation during the combustion experiments with scrap and salt resulted mainly from the organic coatings of the UBC (Table 1). The carbon content of the salt was small (0.031 %) compared with that of the UBC (1.6 %). Both materials contained catalytic elements like copper and iron.

Table 1: PCDD/F concentrations in thermal experiments with aluminium scrap and salt (800 °C).

Exp. No.	material	reaction time, atmosphere	PCDD/F (pg/sample)
1	2 g UBC ^a + 2 g salt ^b	15 min, air	1500
2	2 g aluminium ^c (blank experiment)	15 min, air	n.d.
3	2 g aluminium + 2 g salt	15 min, air	51
4	2 g UBC	15 min, air	733
5	2 g UBC + 2 g salt	2 h, nitrogen	280
6	soot from No. 1	2 h, air	6080
7	residue from No. 1	2 h, air	79
8	2 g UBC + 2 g salt	2 h, air	75200

^a used beverage cans (UBC)

^b melting salt: mixture of NaCl and KCl as main components

^c technical aluminium without organic attachment

The organic material was not completely burned out in the experiments. Unburned material deposited in the quartz tube in the outlet zone of the furnace. It seems that PCDD/F could be formed from this material by de novo synthesis. The residue from a 15 min experiment (No. 7) produced only a small amount of PCDD/F whereas the deposited material formed much more PCDD/F (No. 6). The increase of PCDD/F formation with reaction time (No. 1, 8) was similar to the de novo experiments with fly ash. Pyrolysis of scrap coated with organic material prior to the melting process could reduce the PCDD/F emission. The homologue patterns of de novo experiments, combustion experiments as well as fly ash from baghouse filter and emissions from the pilot-scale plant showed higher PCDF than PCDD concentrations (Figure 2). With increasing degree of chlorination, the content of PCDF decreased. The maximum of PCDD was between the tetra- to hexachlorinated homologues. The isomer patterns (not shown) were similar to other combustion samples [4]. The patterns of the precursor experiments were different. Mainly OCDD was formed. Additional fly ash samples including those from a full-scale plant showed different homologue patterns compared to the patterns presented in Figure 2. These fly ash samples will be investigated to find out the specific mechanisms of PCDD/F formation in aluminium processes.

Acknowledgements

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