Laboratory studies on formation and minimisation of polychlorinated dibenzodioxins and -furans (PCDD/F) in secondary aluminium process

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1. Introduction

Technical thermal processes like municipal and hazardous waste incineration are the main sources for formation and emission of polychlorinated dibenzodioxins/polychlorinated dibenzofurans (PCDD/F) into the environment (Fiedler, 2007), besides of hospital waste incineration (Mininni et al., 2007). Various metallurgic processes like aluminium and copper refineries play also an important part in the overall mass balance for PCDD/F (Bruzzy and Hites, 1996; Buekens et al., 1998; Fiedler, 2007). A PCDD/F emission inventory for 17 western EU countries was published in 2004, iron ore sintering was the second most important source after municipal waste incineration (Quass et al., 2004). But this report stresses the fact that data for other metal industries are still missing. In normal incinerators PCDD/F are emitted by chimneys in the exhaust gases of the incineration plants and can be measured by standard analytic techniques in the stack gas. However, in metallurgic processes PCDD/F are partly eliminated in metallic refineries into the surrounding air and atmosphere of the plants without extensive cleaning devices like performed in municipal waste incinerators. A typical diagram of an aluminium plant is given by Kaune, it shows that partial cleaning of the stack is performed by collection fly ash in a bag house filter. PCDD/Fs can be formed in the melt, which can be partly emitted into the surrounding atmosphere (Kaune et al., 1999). Therefore, the pollutants will become partly diluted, resulting in a lower concentration, but the absolute mass values may still be large and important for the overall mass balance of PCDD/F. Some of these pollutants may become distributed by diffuse pathways in improper maintained plants into neighbouring soils and rivers; this effect was shown recently by investigation of sediments of Liaohe river in China (Zhang et al., 2010). It should be mentioned that the workers of the metallurgic plants might become affected by exposure to these pollutants as has been shown recently by an occupational study of the group of Sweetman et al. (2004). The PCDD/F sampling was performed using static and personal air sampling and high exposures of these pollutants were found especially for aluminium recycling sites. Recently, this result was confirmed by cohort study performed in Germany of former workers from a copper recycling plant (Kersten and Bräunlich, 2002). In addition, a survey of temporal PCDD/F emissions of various sources has been investigated for Germany during the time of 1990 until 2004 (UBA, 2010). There it was shown that PCDD/F emissions have significantly reduced from metallurgic plants into neighbouring soils and rivers; this effect was partly cleaned, resulting in a lower concentration, but the absolute mass values may still be large and important for the overall mass balance of PCDD/F. However, this reduction was observed for metallurgic processes like aluminium and copper recycling. In fact, aluminium recovery is an important sustainable recycling method for this metal; in Germany about 96% are produced by this method. Since, the production of aluminium by primary measure from Bauxit causes much more pollution to the environment this process is less sustainable. Therefore, in a
series of former studies we have investigated the emission of PCDD/F in a pilot-plant rotary furnace (Kaune et al., 1999). PCDD/F are supposed to be resulted mainly from organic impurities attached to the aluminium. Most aluminium cans contain plastic labels (coatings from PVC and epoxy resins) on their surface. In the former experiments the secondary measures like constant feeding of Al scrap were investigated, especially the effect the duct configuration in the after burn zone of the pilot plant (Kaune et al., 1999). For further minimisation of PCDD/F the thermal formation mechanisms of these pollutants were studied along with its pattern of PCDD/F isomers (Kaune et al., 1999). Pattern analysis of PCDD/F obtained from various incineration sources has been used to deduce the mechanisms of their formation (Wehrmeier et al., 1998). The relative importance of two alternative pathways, de novo and precursor formation of PCDD/F have been studied by appropriate laboratory experiments (Dickson et al., 1992). The experiments were designated to simulate the conditions of large scale plants. The full understanding of these results will allow further minimisation by primary measures in aluminium recycling processes operated on technical scale as well as in other metal refinery processes.

2. Materials and methods

2.1. Generated samples by laboratory experiments

The laboratory experiments were conducted to estimate the relative importance of the two relevant pathways for formation of PCDD/F, de novo synthesis and precursor pathway, shown for thermal processes (Wehrmeier et al., 1998). The experiments were designed to model the conditions of postcombustion zone of the aluminium smelt. Therefore, all experiments were performed on a BIS-oven (BIS: Bayer, ICI, Shell) under stream of synthetic air at a flow of 50 mL min⁻¹. In this apparatus, described by Lenoir and Kampke-Thiel (1995) the heating block was moved over the quartz valve with a constant and defined speed, modelling the conditions of an incinerator or a metal smeltery. Using a mill (IKA-Universalmühle M20), fly ashes obtained from the baghouse filter obtained from the secondary aluminium smelter were homogenised. Then, the sample was inserted into a quartz tube of the laboratory furnace (Fig. 1) and heated at 300 °C for 10 and 120 min, respectively. The reason selecting this temperature was based on knowledge of PCDD/F formation in the postcombustion zone of incinerators at about 300 °C (Wehrmeier et al., 1998). Finally, the reaction products were trapped in an ice-cooled impinger filled with toluene at the end of the apparatus.

For de novo experiments type I, 2% of activated char coal were added to 1 g of fly ash sample, whereas for the de novo type II 2% of activated char coal and 1% of sulphur were added to 2 g of sample. In order to study the precursor reaction 100 µg 13C₆-pentachlorophenol (PCP) obtained from Promochem was added to the top of the sample. Furthermore, aluminium shredder, called UBC (used beverage cans) with a constant composition of aluminium and carbon and high concentration of organic material (1.6%) obtained from VAW Aluminium AG, Bonn and technical melting salts (technical NaCl + KCl mixture), called Montanal with a very low carbon content (0.031%) was used for the following type eight experiments (Table 1). These experiments were performed to model the PCDD/F formation reactions in the smelt in analogy to the laboratory studies of PCDD/F formed in the postcombustion zone of incinerators. Additionally, samples of 3.3 g Montanal and 0.89 g UBC was heated for 3 h at 800 °C under flow of synthetic air (Experiment 9) and the resulted PCDD/F from chemical analysis and EROD-bioassay were compared.

The laboratory experiments described above rests on the established hypotheses of thermal PCDD/F formation mechanisms developed from experiments for municipal waste incinerators by Vogg and Stieglitz (1986) and by Dickson et al. (1992).

2.2. Determination of PCDD/F

Prior to analysis, the fly ash was treated with diluted HCl, dried and extracted for 24 h with 800 mL toluene. The extracts and the toluene from the impinger as well as the used toluene for apparatus rinsings were combined. 17 13Cl₁₂ PCDD/F congeners were used as internal standards, except for the precursor experiments, in which 37Cl₄-2,3,7,8-TCDD was added prior to extraction. The clean-up procedure and the instrumental analyses were performed according to Simm et al. (2006). In brief, the clean-up included various chromatographic steps using different types of adsorbents (silica, H₂SO₄-treated silica, alumina, florisil). The identification and quantification of PCDD/F was performed by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) by standard methods described in Schramm et al. (1995, 1998). Quality assurance has been published by Henkelmann et al. (1996). In general, the results for PCDD/F were average values for two runs with a mean deviation of ±10%.

2.3. Micro-EROD-bioassay

The Micro-EROD-bioassay complements the chemical analysis and is able to disclose the existence of unknown dioxin-like compounds not targeted by chemical analysis. The sample preparation and extraction procedure were analogues as explained above for the chemical analytical method, however no internal standard of 13C₁₂ PCDD/F congeners was added to the sample. The obtained extract was concentrated to 4 mL and then a clean-up step was carried out on a “sandwich” column. The sample was eluted with 850 mL n-hexane. The eluate was concentrated and transferred to 150 µL DMSO under N₂ stream at 45 °C. Subsequently, the concentrate was eluted to a mixture DMSO/Isopropanol 4:1 as an optimal carrier solvent for the bioassay. The Micro-EROD-bioassay tests for PCDD/F values were performed by the method reported elsewhere (Hofmaier et al., 1998; Schwirzer et al., 1998). The EROD induction caused by sample extracts after 24 h and 72 h of incubation (semi-persistent and persistent compounds, resp.) was compared to the dose-response curve obtained with standards of

![Fig. 1. Scheme of BIS apparatus.](image)
2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). The results were given as ng 2,3,7,8-TCDD I-TEQ per kg sample.

3. Results and discussion

3.1. Overall yield of PCDD/F by de novo-synthesis and precursor synthesis. Dependence of reaction time

In preliminary experiments no PCDD/F were formed with original fly ash sample. The overall yield of PCDD/F in the both experiments such as de novo synthesis and precursor reaction at reaction time 10 and 120 min, respectively is summarised in Fig. 2.

The yield of 13C12-PCDD/F from 13C6-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. The results showed also that the absolute yield for PCDD/F by the precursor formation pathway is much higher compared to de novo synthesis. In general PCDF dominate over PCDD, which is also found in municipal and hazardous incineration. But one has to consider the higher concentration of particulate carbon in the fly ash of the aluminium recycling plant compared to PCP. Vogg and Stieglitz have shown that de novo synthesis of PCDD/F can be important for municipal waste incinerators (Vogg and Stieglitz, 1986). The carbon content in fly ash of aluminium recycling plants are significantly lower compared to that of municipal waste incinerators. The result is similar to conditions, found by Dickson et al. for model fly ash of municipal waste incinerators (Dickson et al., 1992). The time dependence of the alternative pathways, that is their relative kinetic constants and their activation energies plays also an important role. In the beginning the precursor pathway dominates over the de novo pathway, but after 2 h the de novo pathway will become more important for the overall mass balance similar to the results of the Dickson et al. study. Both processes may be considered as viable pathways for PCDD/F formed in aluminium recycling plants.

The results shown in Fig. 2 were reproducible, when another fly ash from the plant was used, nearly the same results were obtained. The copper content of the fly ashes were in the range of 0.1–0.2%. A correlation of copper content and PCDD/F concentration was not found. The results show that formation of PCDD/F in an aluminium plant is similar compared to other thermal processes, PCDF can be minimised by avoiding particulate carbon containing fly ash for longer times in the post-combustion zone of the smelter.

3.2. Determination of biological TEQ-values (EROD-bioassay) complementary to chemical analysis

The results of chemical analysis and the bioassay are summarised in Table 2. The 24 h bioassay results of generated samples shows factor of 1.8 higher results compared to the samples after 72 h incubation. Moreover, higher TEQ-values were found from precursor experiments than those provided from the bioanalytical test. The ratio between the TEQbioassay/72h and the I-TE is about factor of 5.9. The bioanalytical value of the precursor experiment is very close to unity, which means that the chemical analysis of TCDD-like compounds explained the bioanalytical value by the compounds which have been detected (mainly OCDD). The ratios for the de novo experiments are always much higher than unity which points to the existence of unknown compounds with TCDD-like toxicological properties. Also the aluminium experiments show the formation of some unknowns.

![Graph showing yield of PCDD/F (in%) of applied carbon or PCP in de novo and precursor experiments.](image.png)

**Fig. 2.** Yield of PCDD/F (in%) of applied carbon or PCP in de novo and precursor experiments.

### Table 1
Thermal experiments performed on laboratory scale at 800°C.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Material</th>
<th>Reaction time, atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 g UBC + 2 g Montanal</td>
<td>15 min, air</td>
</tr>
<tr>
<td>2</td>
<td>2 g Al^6+ (blank)</td>
<td>15 min, air</td>
</tr>
<tr>
<td>3</td>
<td>2 g Al^6+ + 2 g Montanal</td>
<td>15 min, air</td>
</tr>
<tr>
<td>4</td>
<td>2 g UBC</td>
<td>15 min, air</td>
</tr>
<tr>
<td>5</td>
<td>2 g UBC + 2 g Montanal</td>
<td>2 h, nitrogen</td>
</tr>
<tr>
<td>6</td>
<td>Soot from No. 1</td>
<td>2 h, air</td>
</tr>
<tr>
<td>7</td>
<td>Residue from No. 1</td>
<td>2 h, air</td>
</tr>
<tr>
<td>8</td>
<td>2 g UBC + 2 g Montanal</td>
<td>2 h, air</td>
</tr>
</tbody>
</table>

* Technical aluminium without organic attachment.

### Table 2
TEQ\textsubscript{NATO,CCMS} (ng kg\textsuperscript{-1}) for samples generated by laboratory experiments (120 min) and comparison of bioassay and chemical analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bioassay (24) h</th>
<th>Bioassay (72) h</th>
<th>Chemical analysis PCDD/F</th>
<th>Bioassay (72) h/chemical analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor experiment</td>
<td>8150</td>
<td>2750(^a)</td>
<td>3265.5</td>
<td>0.8</td>
</tr>
<tr>
<td>De-novo synthesis I</td>
<td>325</td>
<td>184</td>
<td>14.5</td>
<td>2.7</td>
</tr>
<tr>
<td>De-novo synthesis II</td>
<td>827</td>
<td>642</td>
<td>155</td>
<td>4.1</td>
</tr>
<tr>
<td>UBC + Montanal (Experiment No. 9)</td>
<td>480</td>
<td>400</td>
<td>45.9</td>
<td>8.7</td>
</tr>
</tbody>
</table>

* Mean value within quadruplicate determinations.

\(^a\) ng sample\(^{-1}\).
3.3. Concentration of PCDD/F in thermal experiments with different Al-scrap and salt additive formed in the BIS furnace

The results of different aluminium scraps treated in the BIS furnace at two different reaction times are summarised in Table 3.

The results show the organic material of UCB can lead to PCDD/F concentration in aluminium smelting process. The organic material (coating of UBC) was not completely burned in laboratory experiments. Unburned material deposited in the quartz tube in the outlet zone of the furnace as black material. It is most likely that PCDD/F can be formed from this material by de novo synthesis. The residue from the 15 min experiment (Experiment No. 7) produced only a small amount of PCDD/F whereas the deposited material (Experiment Nos. 1 and 8) was similar to the de novo experiment with fly ash. Elimination of the organic material (coating) from UCB either by solution in special solvents or by pyrolysis of scrap coated with organic material in separate heating chambers with good ventilation devices prior to the melting process could reduce the PCDD/F emission. As shown by Experiment No. 5 heating of UBC under nitrogen instead of air leads to much lower concentration of PCDD/F compared to heating in air. A pretreatment of UBC in a heating chamber with nitrogen may destroy the organic material efficiently.

Addition of special inhibitors like solid inorganic salts (e.g. (NH₄)₂SO₄) to Montanal, known for PCDD/F reduction in waste incinerators (Pandelova et al., 2009) might now be an alternative, economical method for reduction of PCDD/F in aluminium smelters.

3.4. Concentration and pattern of homologues of PCDD/F from de novo pathway compared to smelting of UCB performed on laboratory scale and fly ash from bag house filter from pilot-scale plant

In a systematic study the homologue pattern of PCDD/F formation from de novo pathway experiment (type I) and experiment 4 of UCB smelting on laboratory scale and fly ash from bag house filter from pilot-scale rotary furnace of VAW aluminium AG (Kaune et al., 1999) are presented in Fig. 3.

All samples showed higher PCDF than PCDD concentrations, which is also found in waste incinerators. Nearly same concentration of PCDD/F and a similar profile the homologues were found for the three samples (Fig. 3). Therefore, formation mechanisms are likely the same in laboratory de novo experiment and in smelting of UCB and in the bag house of the pilot plant. With increasing degree of chlorination, (increasing number of chlorine atoms in the two organic skeletons) the content of PCDF decreased. The increase of PCDD/F concentration in longer reaction time is similar as observed in former experiments by Dickson et al. (1992) for de novo experiments with fly ash and activated char coal.

The homologue profile in the precursor experiments is different from the de novo experiments in aluminium smeltery experiments. Here, mainly OCDD is formed by an Ullmann type II condensation of PCP. From municipal waste incineration it is known that lower chlorinated PCDD are formed from higher chlorinated one by the

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**Table 3**

PCDD/F concentration in thermal experiments with Al scrap and salt at 800 °C.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>PCDD/F (pg sample⁻¹)</th>
<th>Experiment No.</th>
<th>PCDD/F (pg sample⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1500</td>
<td>4</td>
<td>733</td>
</tr>
<tr>
<td>2</td>
<td>n.d.</td>
<td>5</td>
<td>280</td>
</tr>
<tr>
<td>3</td>
<td>51</td>
<td>6</td>
<td>6080</td>
</tr>
<tr>
<td>4</td>
<td>733</td>
<td>7</td>
<td>79</td>
</tr>
</tbody>
</table>

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**Fig. 3.** Concentration and homologue pattern of PCDD/F formed by de novo experiments (type I), UCB smelting (Experiment No. 4) and fly ash sample from baghouse filter of a pilot scale (Kaune et al., 1999).

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**Fig. 4.** Relative TCDD-pattern (TCDD/sum TCDD) in aluminium recycling processing.
3.5. Ratio of regio-isomers of TCDDs formed in the aluminium smelting process

Wehrmeier et al. found that the 18 regio-isomers of TCDD are found in a nearly constant ratio of different matrices of various waste and hazardous waste incineration sources, this is the so-called characteristic incineration pattern. Therefore, we subjected this method of determination of regioisomers also to the samples of aluminium smelter, pilot pant as well as from the laboratory experiments, see Fig. 4 and Supplementary data. The pilot plant samples are from reported results by Kaune et al. (1999). The results are useful for a qualitative picture, it shows the similarity of the formed ratio of regioisomers as a typical pattern.

The results show that there is also a characteristic incineration pattern for the tetrachlorinated compounds, TCDD in the aluminium process like in the municipal waste incineration as found by Wehrmeier et al. (1998). The processes for formation of PCDD/F are most likely similar in all thermal processes studied so far.

4. Conclusion

The results show that thermal formation of PCDD/F in aluminium smelters are similar to that found in waste incinerators. Both processes, de novo as well as precursor pathway play an important role depending on conditions like temperature and time. Therefore, primary measures developed for waste incinerators should also be used in metal smelters. Residues in the conduct of the plants containing fly ash with particulate carbon should be cleaned in constant time intervals to avoid the de novo synthesis in this matrix. The input carbon of the recycling metal (lack on the surface) should be reduced to minimise the amount of PCDD/F. Precleaning of organic material of UCB by heating in nitrogen can be an alternative for PCDD/F minimisation. The primary methods developed for PCDD/F minimisation of waste incinerators like constant feeding into the furnace and good heating/burning techniques can also be used for metal smelters, as it was shown recently by Holtzer et al. (2007) and also by Lv et al. (2011). The complementary investigation of chemical and biological determination of TCDD-like compounds points to the existence of unknown bioactive compounds in case of de novo experiments and pilot scale smelting.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2011.11.014.