THE EFFECT OF MSWI START-UP AND SHUT-DOWN ON CONGENER PROFILES OF PCDD/F PRECURSORS

Šyc Michal[1], Pekárek Vladimír[1], Fišerová Eva[1], Karban Jindřich[1], Punčochář Miroslav[1]

[1]Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, v.v.i., Rozvojová 2, 165 02 Prague 6, Czech Republic

Introduction

A lot of recent studies were concerned with investigating of instationary phases of MSWI plant operation, i.e. its start-up and shut-down[1–9]. These specific phases were studied from the standpoint of stack emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F)[1–4,7–9] as well as with respect to PCDD/F concentrations in raw flue gases[1–8]. However, only limited data have been collected so far on the concentrations of precursor compounds like polychlorinated phenols (PCPh) and polychlorinated benzenes (PCBz)[2,3,5,6,10]. Moreover, in most studies the congener profiles of nontoxic PCDD/F were not presented. The effect of the instationary phase of MSWI operation has only been described for TCDD/F profile[5,6]. In general, the congener profiles of precursor compounds, PCBz and PCPh, were not of much concern. The aim of this work was to find characteristic congener profiles for the steady state incineration regime and to determine changes in PCBz and PCPh profiles under the steady-state and instationary regimes of MSWI operation.

The concentrations of PCBz, PCPh, and PCDD/F in raw flue gases were determined at the outlet of the electrostatic precipitator. The sets of measurements covered the steady state regime, shut-down and start-up of MSWI and the subsequent phase in which memory effect can be expected. The details of MSWI plant were reported elsewhere[10].

Sampling and analytical procedures used for PCBz, PCPh, and PCDD/F determination were made according to the Czech standard ČSN EN 1948. In the following text PCBz stands for the sum of TriCBz to HxCBz and PCDD/F for the sum of TCDD/F to OCDD/F.

Results and Discussion

PCBz in raw flue gases were analysed during three measurement campaigns around three shut-downs. The results are shown in Fig. 1. The PCPh and PCDD/F concentrations in the flue gases were determined only during the third campaign, and the data obtained are shown in Figs. 2 and 3. The first day after the shut-down, PCBz, PCPh, and PCDD/F in the raw flue gases significantly increased, and then gradually decreased. The length of the memory effect period differed, depending on the individual compound studied.

In measurement campaign 1, the day before the shut-down (Day -1), the low PCBz concentrations found were comparable to those for the steady-state regime. Similarly low value in relation to the steady-state regime was observed already in the fourth day after the shut-down (Day 4). The last day before the shut-down of measurement campaign 2, PCBz concentration in the raw flue gases attained the lowest value of all the measurements. The fourth day after the shut-down, the PCBz concentration in the flue gases decreased to the value of the steady-state regime. The last day before the shut down in measurement campaign 3 (Day -1 C3), the flue gases contained the highest PCBz concentration, due to the removal of the incrustations deposited in the boiler by controlled explosions of an ethane-oxygen mixture. In this process a special glass balloons containing this mixture were introduced during incineration to the critical sites containing large amounts of the incrustations, and then the mixture was ignited with electric discharge. Apart from the short-time distortion of the steady state regime of MSWI operation, the large amounts of solid fly ash particles are released to the flue gases. The first day after the shut-down of measurement campaign 3, PCBz concentration in flue gases was the second highest observed. The PCBz concentrations higher than in the steady-state regime were found even on the sixth day after the shut-down. The above mentioned data demonstrate that the length of the memory effect is largely affected also by the phase preceding the shut-down. The shut-down of MSWI with emphasis on the minimalization of POP formation leads also to the suppression of their formation during the restart of combustion process as well as to the shorter memory effect.

Figs. 1–3 illustrate the different length of the memory effect for PCDD/F and their precursors, PCBz and PCPh. While for PCBz and PCPh their increased concentrations were observed even the sixth day after the shut-down, PCDD/F concentrations were the same as at the steady-state regime.

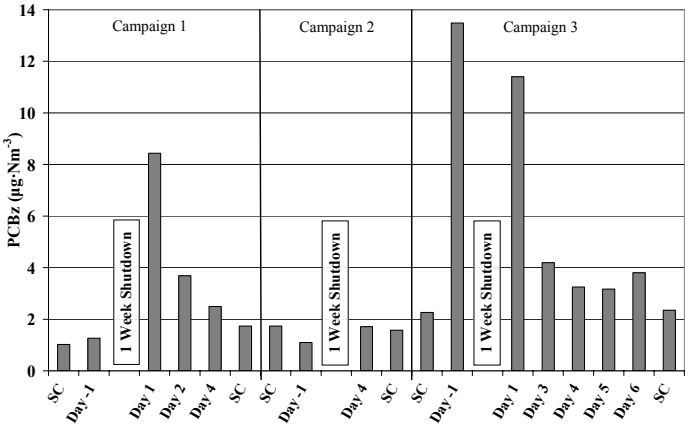

Fig. 1 PCBz concentrations in raw flue gases
SC - steady-state regime

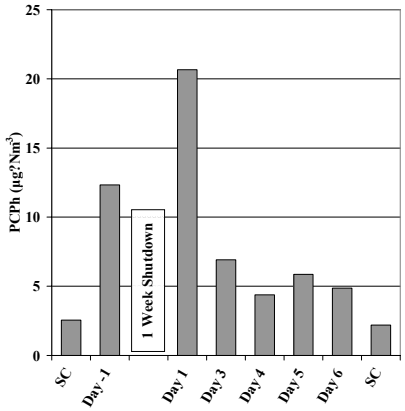

Fig. 2 PCPh concentrations in raw flue gases

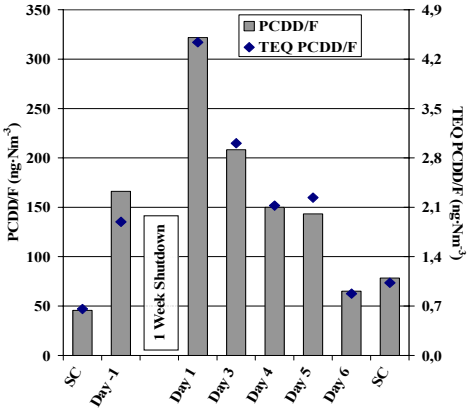

Fig. 3 PCDD/F concentrations in raw flue gases

Congener profiles of PCBz and PCPh

PCBz congener profiles differ for the steady-state and instationary regime of the incineration plant operation. Very similar profiles were, however, found for the steady-state regime and for memory effect phases, as supported also by the low standard deviations (n=19) in Fig. 4. A more detailed investigation was performed for the ratios of TriCBz and TCBz congeners, since the overall PCBz congener profile is affected also by changes of chlorination-dechlorination equilibria. It was found that the ratios of TriCBz and TCBz congeners do not vary during the steady-state regime or memory effect phase. Similar TriCBz and TCBz ratios in the flue gases were also found the last day before the shut-down (for campaign 1, 2). Different TriCBz and TCBz congener ratios in the flue gases were observed the first day after the shut-down as well as the last day before the shut-down in measurement campaign 3 which included the explosive removal of the boiler incrustations. The experiments with the different congener profile were characterized also by the increased PCBz concentrations in the flue gases. In the case of the explosive deposit removal, the increased amounts of ash particles can be expected. In the initial phase of the start-up of MSWI, the combustion chamber is first heated by combustion of an auxiliary fuel (natural gas) to the temperature above 850 ºC.

During this period the post-combustion parts of the incineration plant with deposited fly ash are gradually warmed up. From automatic monitoring of combustion chamber temperatures it follows that the temperature window in which de novo synthetic reactions are taking place lasts for 3.5 h. During the combustion of natural gas, the formation of PCDD/F in the gas phase or a significant precursor formation cannot be expected. After the temperature of 850 ºC was attained, the feeding of waste is started. Apart from PCDD/F and its precursors formation from waste combustion, the formation of PCDD/F and their precursors during heating up the incinerator that are formed from the ash deposited on its walls should also be considered. A characteristic feature of both cases in which the change of TriCBz and TCBz was detected was the increased effect of ash particles and/or an increased ash concentration in the flue gases. The shift of the congener profiles resulted from a decreased proportion of 1,3,5-TriCBz, 1,2,4-TriCBz and 1,2,4,5-TCBz and an increased proportion of 1,2,3-TriCBz and 1,2,3,4-TCBz (see Fig. 5 and Fig. 6).
In laboratory experiments[11], a sample of MSWI fly ash cleaned by extraction and thermal treatment was heated in the presence of the reaction components of de novo synthetic reactions. This treatment eliminated the precursors present in the ash sample and minimized their entrance to the reaction system. The ratio of TriCBz formed, [1,3,5-TriCBz]:[1,2,4,5-TCBz]:[1,2,3-TriCBz] was 0.3:11.9:87.8 and that of TCBz congeners [1,2,3,5-TCBz]:[1,2,4,5-TCBz]:[1,2,3,4-TCBz] was 25:10:65. As the purification removed the precursors from the ash sample, the above PCBz congener profiles result from the de novo synthetic reaction taking place during heating of the fly ash. We thus believe that the amount of ash in the reaction system affects PCBz congener profile.

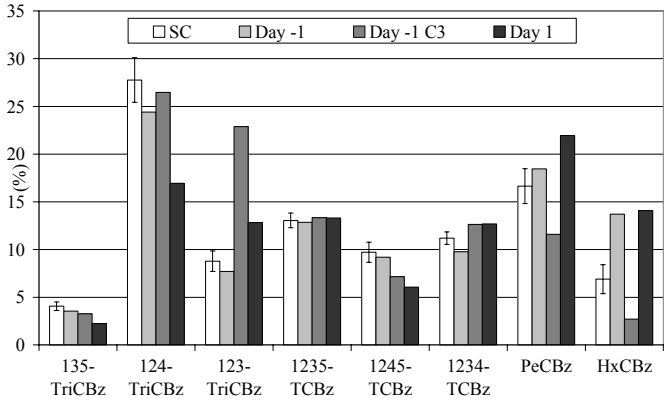

Fig. 4 Congener profiles of PCBz
Day -1 C3 - last day before shut-down, campaign 3

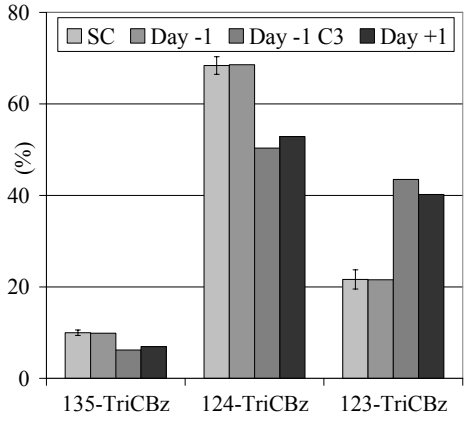

Fig. 5 Congener profiles of TriCBz

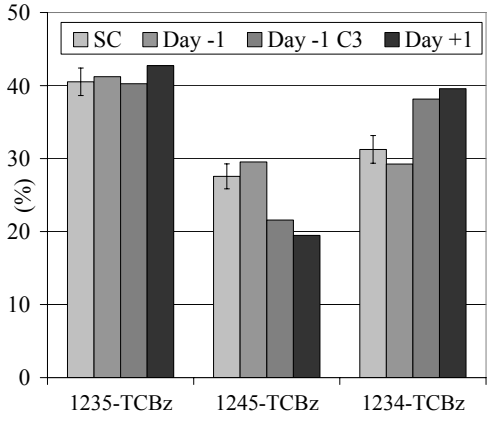

Fig. 6 Congener profiles of TCBz

By contrast, the typical congener profile of PCPh was not found. The sum of the congeners corresponding to the chlorination model of PCPh formation from phenol, namely the so called 2,4,6-congeners (2-MCPh, 4-MCPh, 2,4-DiCPh, 2,4,6-TriCPh, 2,3,4,6-TCPh, and PeCPh) was followed, amounting to 75 to 94 % in the raw flue gases (n=11, median 87 %), except one experiment at the steady state combustion regime where this sum was only 49 %. In this experiment the sum of 3,4,5-congeners (3-MCPh, 3,5-DiCPh, 3,4,5-TriCPh, and 2,3,4,5-TCPh) was 20 %, in the other 11 experiments it amounted to max. 8 %. The specific feature of the congener profile was apparent also from the proportion of the other congeners. 2,3,5,6-TCPh formed 16 % of all PCPh, in the other 11 experiments its proportion did not exceed 1 %. Analogously, the proportion of 3,4,5-TriCPh was 11 % and in the other experiments less than 1 %. To identify the reason of these changes is difficult at present. Most likely it seems that it is the change of reaction conditions or the entrance of some compound to the reaction system in the incinerated waste that affects the regioselectivity of the chlorination. Another reason may be the content of phenolic and phenol-like compounds in the incinerated waste and thus a different mechanism of PCPh formation in this experiment. The congener profile of PCBz did not differ from the "normal" profile found in the steady-state incineration regime. This implies a different mechanism of PCBz and PCPh formation, since in this experiment the orientation of chlorination of PCBz was not changed. Any clear-cut effect of the incineration regime on PCPh congener profile has not been detected, although the experiments with high total PCPh concentration (the first and last day around the shut-down) showed also the higher proportions of 2,4,6-PCPh congeners. For comparison, in the fluidized bed combustion[12] the sum of seven 2,4,6-PCPh congeners amounted to 99 %, demonstrating thus the dominant PCPh formation via chlorination path. On the other hand, in none of 12 experiments performed, such a high value was found by us in the flue gases of the incinerator equipped with a stoker fired furnace used in the present study.

Acknowledgments
This work could not have been realized without financial support of the Ministry of Education, Youth and Sports granted within the framework of the programme Eureka (Projects IP04OE156 and OE200) and the programme Health and life quality (Project WARMES 2B08048).

References

1. Gass HC, Lüder K, Wilken M. *Organohalogen Compounds*, 2002, 56:193
2. Gass HC, Lüder K, Sünderhauf W, Wilken M. *Organohalogen Compounds*, 2004, 66:935
3. Gass HC, Wiken M, Lüder K. *Organohalogen Compounds*, 2003, 63:25
4. Wilken M, Marsch F, Dehoust G. *Organohalogen Compounds*, 2003, 63:29
5. Neuer-Etscheidt K, Orasche J, Nordsieck H, Streibel T, Zimmermann R, Kettrup A. *Chemosphere*, 2007, 67:S205
6. Neuer-Etscheidt L, Nordsieck H, Liu Y, Kettrup A, Zimmermann R. *Environ. Sci. Technol.*, 2006, 40:342
7. Grosso M, Cernuschi S, Giugliano M, Lonati G, Rigamonti L. *Chemosphere*, 2007, 67:S118
8. Tejima H, Masahide N, Yasuyuki F, Matsumoto A, Takeda N, Masaki T. *Chemosphere*, 2007, 66:1123
9. Wang LCh, Hsi HCh, Chang JE, Yang XY, Chang-Chien GP, Lee WS. *Chemosphere*, 2007, 67:1346
10. Šyc M, Pekárek V, Fišerová E, Punčochář M, Karban J, Prokeš O. *Organohalogen Compounds*, 2006, 68:1232
11. Pekárek V, Weber R, Grabic R, Šolcová O, Fišerová E, Šyc M, Karban J. *Chemosphere*, 2007, 68:51
12. Weber R, Hagenmaier H. *Chemosphere*, 1999, 38:2643