

PCDD/PCDF Formation in Fluidized Bed Incineration

Roland Weber^a and Hanspaul Hagenmaier^b

^aResearch Institute, Ishikawajima-harima Heavy Industries Co.,Ltd., 1, Shin-Nakahara-cho, Isogo-ku, Yokohama 235, Japan

^bInstitute of Organic Chemistry University of Tübingen, D-72076 Tübingen, FRG

INTRODUCTION

As early as 1984 it was recognized that PCDD/PCDF emission patterns of municipal waste incinerators (MWI) were very similar [1]. This led to the assumption that the route of formation of PCDD/PCDF in these incinerators must also be similar. Later it was found that these isomer distribution pattern are rather characteristic for the formation of PCDD/PCDF in thermal reactions.

The waste incinerators which were investigated for PCDD/PCDF emissions in Europe, the United States and Canada were practically all equipped with grate firing. While in these countries until recently this was the only technology used for waste incineration, in Japan a large number of fluidized bed incinerators (FBI) are in operation since many years. Here the waste is decomposed and gasified in an air bubbled sand bed at 650-750° C and the resulting volatile compounds are burned in the secondary combustion chamber for more than two seconds at about 900°C to promote completion of combustion. In Europe this technology has been used mainly for incineration of sewage sludge. In the last two years three FBIs for municipal waste are being constructed or are already in operation in Spain, the UK and in Germany.

About 10 years ago it was reported that higher levels of PCDD/PCDF are generated in FBI in comparison to other types of incinerators [2]. Newer types of FBIs can fulfill the stringent limiting value for PCDD/PCDF emission of 0.1 ng I-TEQ/Nm³ [3,4] which has been in effect in Japan since January 1997 for all new waste incinerators [5].

There have been no reports in the literature whether the isomer distribution pattern of PCDD/PCDF in filter dust and stack gas of FBIs are identical to those of other types of incinerators.

Studies on the PCDD/PCDF formation in FBIs are of interest, because they can serve as a basis for minimizing PCDD/PCDF formation and emission, especially in older facilities. They also might yield further insight into the basic mechanism of PCDD/PCDF formation.

METHODS

Sampling: For facility A, samples of the flue gas were taken before the electrostatic precipitator (EP) and after the electrostatic precipitator. For the 9 other facilities only stack gas and fly ash samples were analyzed.

Sampling for PCDD/PCDF was carried out according to the procedure of the Japanese Waste Research Foundation [6]. The ^{13}C -PCDD/PCDF standards were added to the XAD prior to sampling.

For facility A, chlorobenzenes and chlorophenols were sampled with two impingers in series, filled with toluene and kept at 0°C. The ^{13}C -labeled standards were added to the toluene prior to sampling.

Clean-up: The clean-up procedures are described elsewhere [7].

Analysis: The actual analysis was carried out on a HP 6890 gas chromatograph coupled to a HP 5973 mass selective detector.

Quantification was carried out by isotope dilution mass spectrometry. For each degree of chlorination (PCDD/PCDF, PxCBz and PxCBz) at least one ^{13}C -labeled standard was added after sampling.

RESULTS

The PCDF isomer distribution pattern found in flue gas and fly ash samples of the fluidized bed plant A (Figure 1) are distinctly different from those found in hundreds of fly ash and flue gas samples from a number of grate fired incinerators ("stoker" type) from Europe, and also different from PCDF isomer distribution pattern found in ambient air samples from various parts of Germany. In stack gas samples of 9 other fluidized bed incinerators of the same manufacturer the same isomer distribution pattern was found in three of the installations while in the six other incinerators a "mixture" of this "extreme fluidized bed" type pattern and the usual "stoker" type pattern was found. In Figure 2 the mass fragmentograms of tetraCDFs are shown for plants A-D, E-G and H-J. An increasing tendency towards the stoker type pattern can be recognized.

There is no strict correlation between absolute concentrations and isomer pattern. Plant A had an emission of 50 ng I-TEQ/m³ (the highest measured in this series) and plant E an emission of 0.1 ng I-TEQ/m³ (the lowest measured in this series).

Description of PCDD/PCDF isomeric pattern

PCDD pattern

In incinerators of the stoker type, two different patterns for the tetra- and pentaCDD can be distinguished [8]. In one pattern 1,3,6,8- and 1,3,7,9-T₄CDD dominate the T₄CDD and x,x,x,6,8- and x,x,x,7,9-P₅CDD dominate the P₅CDD (2,6-PCDD pattern). The other pattern is characterized by formation of all isomers to an almost equal amount, and the formation of the 2,3,7,8-substituted isomers is not discriminated (2,3-PCDD pattern). Both patterns can be found in the same in incinerators at different places [9] and there can be seen a continuous change from one pattern to the other.

The PCDD pattern found in the fluidized bed incinerator A both at the inlet and the outlet of the EP corresponds to an extreme 2,6-PCDD pattern. The same is true for the incinerators B-G. However, in plants H, I and J the 2,3-PCDD pattern is partially seen.

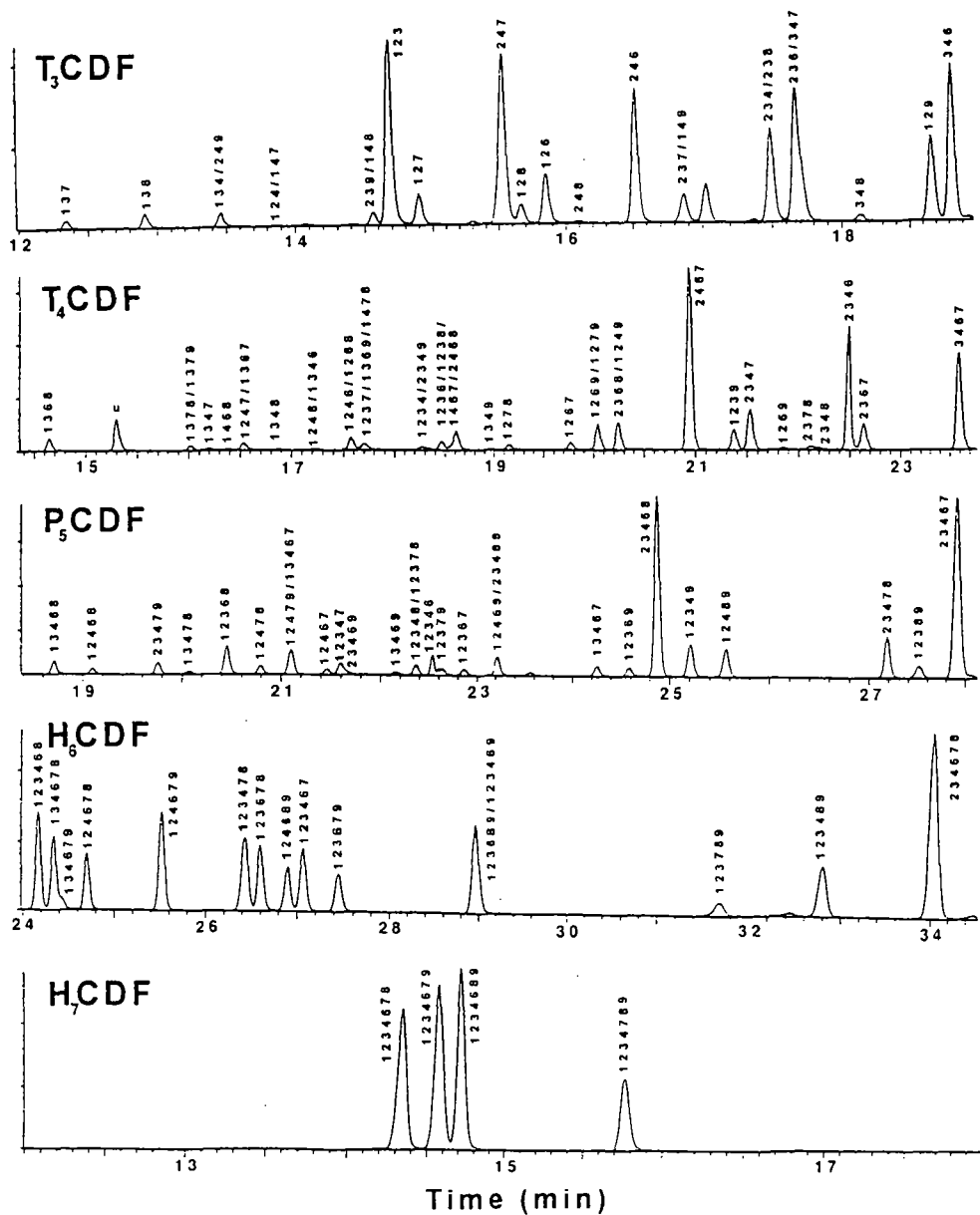


Figure 1: "Extreme fluidized bed" pattern of T₃CDF-H₇CDF in stack gas and fly ash samples of plant A-D (GC-columns: T₃CDF-H₆CDF on Sil-88, H₇CDF on DB-5)

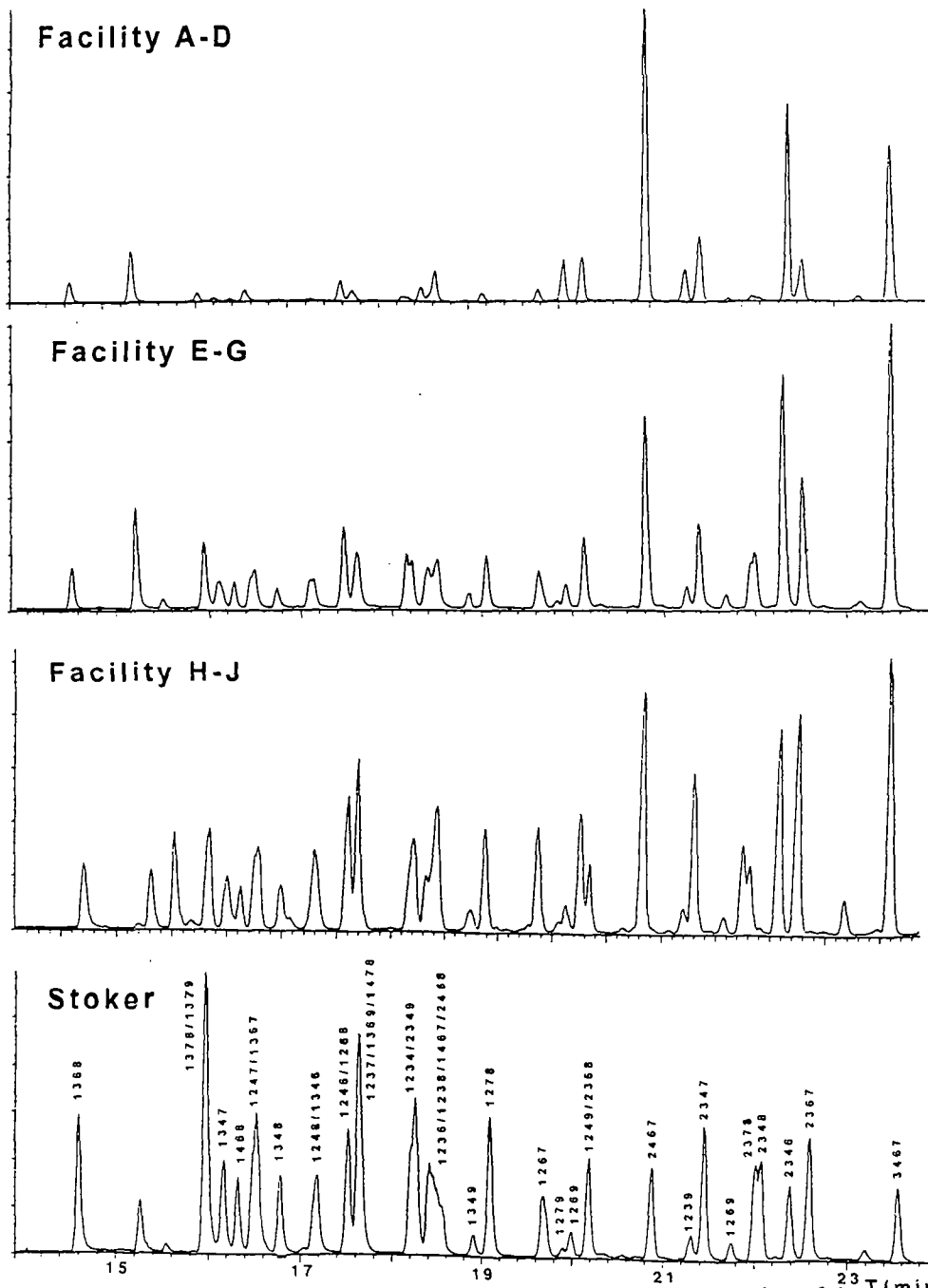


Figure 2: T₄CDF isomer pattern of fluidized bed MWIs (A-J) - conversion of the "extreme fluidized bed" pattern towards the "stoker" pattern

2,3,7,8-Substituted Congener profiles

As a consequence of differences in the isomer pattern found for both PCDD and PCDF between fluidized bed samples and stoker samples the profiles of 2,3,7,8-substituted congeners differ for these samples. The 2,6-PCDD pattern results in low concentration of 2378-T₄CDD and 12378-P₅CDD, and therefore the PCDF in FBIs account for more than 80% of the I-TEQ.

PCDF isomer pattern

The average isomer distribution pattern found in stoker type incinerators exhibits for the tetra-, penta- and hexaCDF the formation of a large number of isomers in comparable concentrations. However, with the H₇CDF the 1234678-substituted isomer predominates with about 70% of the total H₇CDF concentration.

Compared to the stoker type isomer distribution pattern, the PCDF pattern in the extreme fluidized bed is almost complementary (Figure 1). All 4 H₇CDF isomers are formed in similar concentrations. However, only a few tetra- and pentaCDF isomers are formed. For the tetraCDF these are the 2467-, 3467-, 2367-, 2346- and 2347-T₄CDF. Together they amount to about 70% of the 38 T₄CDF isomers. The isomers most typical for the usual fly ash pattern are only minor components. With pentaCDF the three isomers 23468-, 23467-, and 23478-P₅CDF represent more than 50% of the 28 isomers. Again the most prominent isomers of the stoker type pattern are almost completely missing. The H₆CDF show "abnormalities" with a relatively high abundance of the 124679-, 124689-, 123689-/123469- and 234678-H₆CDF.

The homologue profile of the fluidized bed sample also shows some difference to the stoker type in so far as the maximum is seen with the H₇CDF while it is usually found with the tetra- or pentaCDF. On the average, a higher degree of chlorination is observed for the PCDF and a lower degree for PCDD.

Interpretation of PCDD/PCDF isomer pattern with regard to formation mechanism

The 2,6-pattern found in the fluidized bed samples can be derived by condensation of chlorophenols [8]. A detailed analysis of the PCDD isomers found shows a perfect correlation with the chlorophenol congeners found in the fly ash.

The well known PCDF isomer distribution pattern of grate fired incinerators shows a discrimination of 1,9-substituted congeners which is most obvious for the hexa- and heptaCDF. However the absence of this structural element is characteristic also for the tetra- and pentaCDF. The reason is the thermodynamic instability of this structural element. The explanation for the stoker pattern could be a thermodynamic control of the PCDF formation e.g. via chlorination/dechlorination.

In fluidized bed incinerators the 1,9-substituted congeners are not discriminated. Together with the discrimination of the 2,3,7,8-T₄CDF this is a further proof that this isomer distribution pattern cannot result from chlorination of dibenzofuran or dechlorination of PCDF, regardless whether free or imbedded in the carbon particulate matrix. Here the observed substitution pattern is governed by the substitution pattern of intermediate chlorophenols and chlorobenzenes.

CONCLUSIONS

There is a distinct difference in PCDD/PCDF isomer distribution pattern in fly ash and stack gas from fluidized bed incinerators and grate fired incinerators. This is explained by a difference in the mechanism of formation due to a difference in fly ash composition. The elementary analyses

of fly ash from fluidized bed incinerators show a comparatively high content in Ca (16-25%) and Fe (4-11%). The high calcium content is due to the injection of either $\text{Ca}(\text{OH})_2$ or CaCO_3 for removal of HCl and SOx. This is accomplished by either direct injection of CaCO_3 into the combustion chamber (at about 850°C) or by injection of $\text{Ca}(\text{OH})_2$ into the flue gas (at about 350°C). The most extreme "fluidized bed type" isomer distribution pattern is found in those incinerators where CaCO_3 is injected directly into the combustion chamber (plant A-D). Plants G-J are those where $\text{Ca}(\text{OH})_2$ is injected into the flue gas.

The pH of the fly ash samples from the fluidized bed incinerators is rather high. Injection of CaCO_3 into the combustion chamber yields fly ash with a pH of 11-12.5, injection into the flue gas at 350°C fly ash with a pH of 10-12. Whether this highly alkaline matrix drives the condensation of chlorophenols to yield the extreme 2,6-PCDD isomer pattern and at the same time the condensation of chlorophenols with chlorobenzenes resulting in the specific PCDF isomer pattern has to be investigated further in laboratory experiments.

ACKNOWLEDGMENTS

The authors would like to thank Takeichi Kondo for sampling and Makoto Miki for detailed information about the investigated facilities.

REFERENCES

- [1] A. Nottrodt, K.D. Sladek, W. Zoller, H. Buchert, Th. Class, W. Krämer, R. Kohnle, H. Magg, P. Mayer, M. Swercv and K. Ballschmitter, *Müll und Abfall*, **1984**, 16, 313.
- [2] M. Hiraoka et al.. A study on the Formation and Decomposition Mechanisms of Dioxins and Related Compounds, *Environmental Research in Japan*, 2 (1986).
- [3] R. Ishikawa, A. Buekens, H. Huang and K. Watanabe, *Organohalogen Compounds*, **1997**, 31, 512.
- [4] T. Watanabe, M. Asai, T. Kondo, M. Shimizu, Y. Takeuchi, H. Aramaki and M. Naito, *Chemosphere*, **1996**, 32, 177.
- [5] The Advisory Committee for Controlling PCDDs/DFs in MSW Management. Guidline for Controlling PCDDs/DFs in MSW Management, 1997.
- [6] Japanese Ministry of Health and Welfare, A standard manual for analysis of polychlorinated dibenzo-p-dioxins and dibenzofurans in MSW control, Feb. 1997.
- [7] J. Höckel, L. Düsterhöft, W. Körner, and H. Hagenmaier, *Organohalogen Compounds*, **1995**, 23, 139.
- [8] K. Ballschmitter, R. Bacher, Chapter 4.2, p. 92-114, in *Dioxine*, VCH Verlagsgesellschaft mbH, Weinheim, **1996**, ISBN 3-527-28768-X.
- [9] T. Yamoto, S. Inoue, and M. Sawachi, *Chemosphere*, **1989**, 19, 271.