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FORMATION OF POLYCHLORINATED DIOXINS AND DIBENZOFURANS IN INCINERATION OF RDF AND PULP AND PAPER MILL BIOSLUDGE

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ABSTRACT
Incineration tests of refuse derived fuel (RDF) and biosludge were performed in a pilot scale circulating fluidized bed plant. Organochlorinated compounds and metals were analyzed in fuel material, flue gas and fly ash. Post-formation reactions of polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF) were due to fuel material, specially the concentrations of chlorine and metals in fuel. Combustion conditions like distribution of fuel feed rate and carbon monoxide in flue gas also had an effect on levels of PCDD/PCDFs. The clorination of PCDD/PCDFs were observed to take place already at high temperatures in the combustor.

INTRODUCTION
Municipal waste incinerators emit chlorinated dioxins, chlorinated furans and their possible precursors, like chlorophenols. Formation mechanism of PCDD/PCDFs have been reported as formation from precursors and as de novo synthesis from chlorinated organic compounds, catalysts and chlorine[1,2,3,4]. PCDD/PCDFs formation reactions in incineration have been proposed to promote by metals[5,6,7]. The high concentrations of metals, chlorine and the variation of RDF fuel material can lead to PCDD/PCDF formation.

PCDD/PCDF compounds have also been reported to form during chlorobleaching of pulp. Toxic chemicals have been observed to form specially when chlorine has been used as the chlorobleaching chemical[8]. Organohalogen compounds are transported from the process to mill effluents. Many organochlorines, like chlorophenols, chloroguaiacols and chlorocatechols are reported to be bound chemically to organic matter[9]. Waste water treatment plants remove part of organochlorines from effluent to waste sludges. By incineration of RDF and biosludge these toxic chemicals can be emitted to environment.

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EXPERINMENTAL PROCEDURE

Three fuel mixtures were incinerated: two tests of biosludge plus bark (tests 1, 2), three tests of biosludge plus wood chips (tests 3,4,5) and two tests of RDF (tests 6,7). In the RDF incineration test the sampling of chlorinated organic compounds was carried out simultaneously at three sites of the process. In the sludge incineration tests sampling was performed at two sites of the process. Sampling points were after the hot cyclone (AHC), before the baghouse (BBH) and after the baghouse (ABH). Flue gas temperatures in these sampling points were about 850°C, 250°C and 200°C. The introduction of the pilot plant and the sampling points of flue gases are presented in Figure 1.

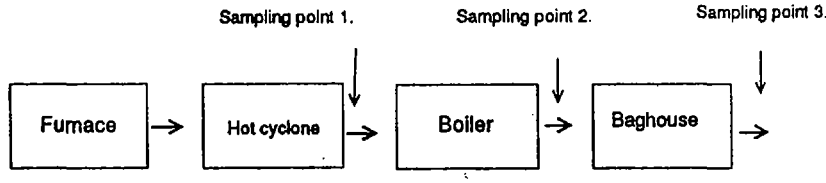

Figure 1. The introduction of the pilot plant and the locations of sampling points.

Sampling was carried out isokinetically. Total glass or quartz probes and sampling units were used. Particles were separated by glass fiber filters and gasous compounds were adsorbed onto XAD-2 resin. A pressurized air cooled probe system was used in the hot flue gas sampling point (AHC).

RESULTS AND DISCUSSION

In RDF incineration PCDD/PCDF concentrations formed in furnace were high. In the similar way the post-formation of PCDD/PCDFs was observed. High concentrations occurred in the furnace, because of the high content of chlorine in fuel. The explanation for the high post-formation rate could be the high metal concentrations in fuel, fly ash and flue gases. Furans were present in higher concentrations than dioxins.(Figure 2.)

Chlorination of dioxin and furan congeners took place already in the furnace at high temperatures. The isomeric distribution was quite independent of the sampling location. Variations of different congeners of PCDD/PCDFs were quite small between the sampling points. The biggest variation was observed in RDF incineration tests, specially for tetra-furans. That could be a consequent of high metal concentrations in flue gas and large variation of fuel quality. (Figure 3. and 4.)

To conlude, the post-formation reactions of PCDD/PCDFs did depend on fuel material chlorine contents. The chlorination took place at high temperature area. The amounts of specific substituted dioxins and furans increased or decreased between the sampling points effected by activators (metals, chlorine).

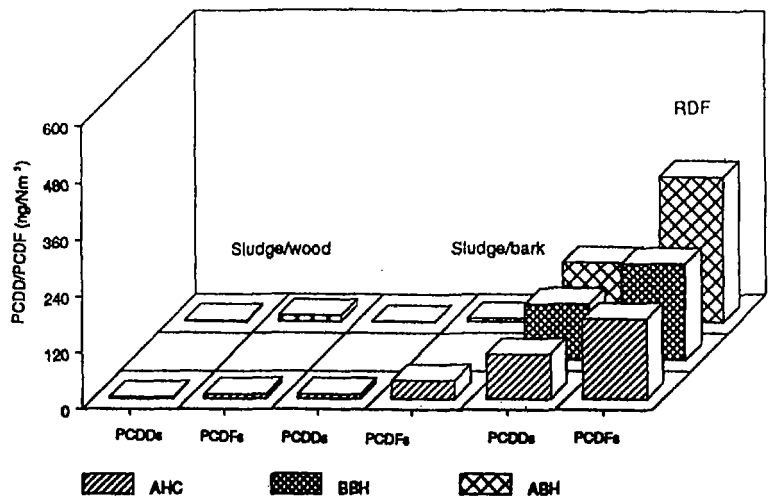

Figure 2. PCDD/PCDF levels in flue gases in the incineration tests of RDF and biosludges

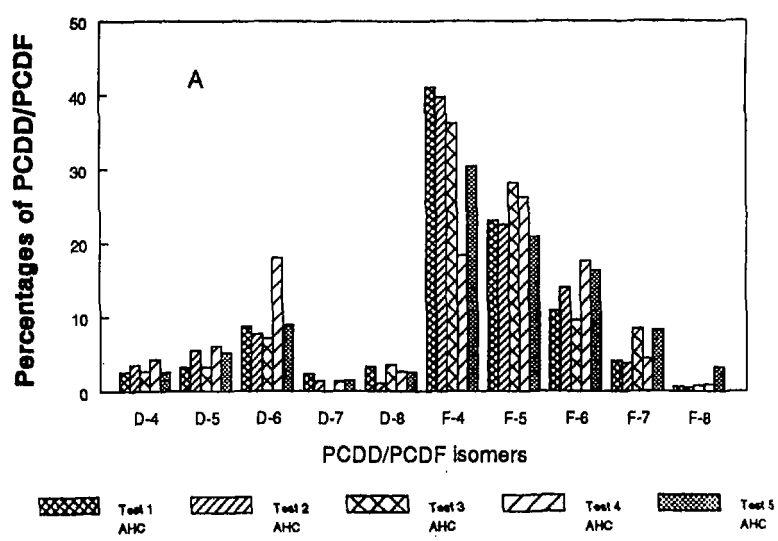

Figure 3 a) The isomeric distributions of PCDD/PCDFs measured in flue gas in different location of process (biosludge tests in AHC).

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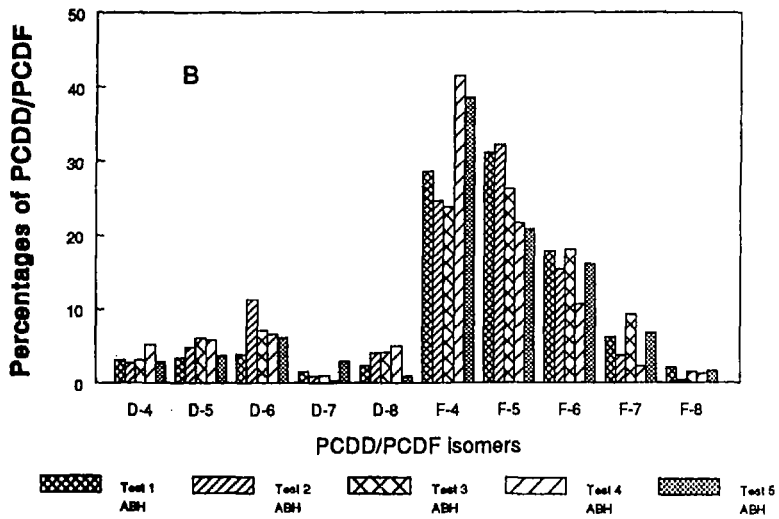

Figure 3 b) The isomeric distributions of PCDD/PCDFs measured if flue gas in different location of process (biosludge tests in ABH).

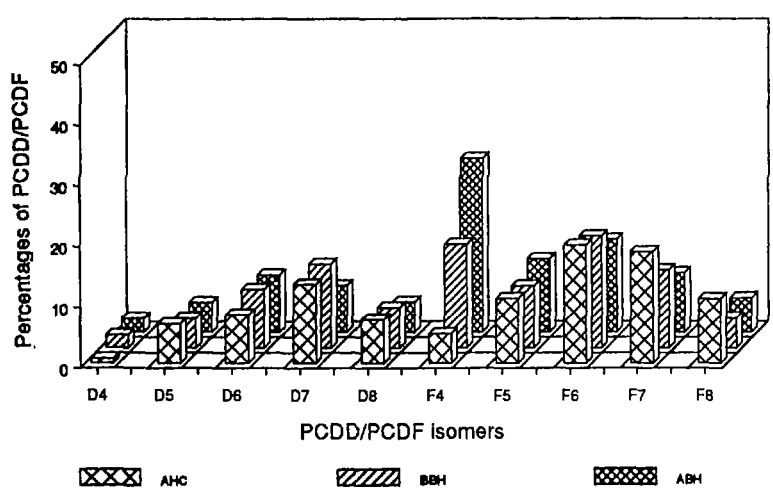

Figure 4. The isomeric distribution of PCDD/PCDFs in RDF tests. The concentrations are aritmetic means of two test.

REFERENCES

1 Karasek, F.W. and Dickson, L.C., Model studies of polychlorinated dibenzo-p-dioxin formation during municipal refuse incineration. Science 1987; 237: 754-756.
2 Gullett, B.K., Bruce, K.R., Beach, L.O., Formation of chlorinated organics during solid waste combustion. Waste Management & Research 1990; 8: 203-214.
3 Hagenmaier, H., Kraft, M., Brunner, H., Haag, R., Catalytic effects of fly ash from waste incineration facilities on the formation and decomposition of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. Environ. Sci. & Technol. 1987; 21: 1080-1084.
4 Stieglitz, L., Zwick, G., Beck, J., Roth, W., Vogg, H., On the de-novo synthesis of PCDD/PCDF on fly ash of municipal waste incineration. Chemosphere 1989; 18: 1219-1226.
5 Stieglitz, L., Vogg, H., On formation of PCDD/PCDF in fly ash from municipal waste incinerators. Chemosphere 1987; 16: 1917-1922.
6 Hinton, W.S. and Lane, A.M., Characteristics of municipal solid waste incinerator fly ash promoting the formation of polychlorinated dioxins. Chemosphere 1991; 22: 473-483.
7 Gullett, B.K., The effect of metal catalysts on the formation of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran precursors. Chemosphere 1990; 20: 1945-1952.
8 Daube, A.K., Karlm, M.R., Dimmel, D.R., McDonough, T.J., Banerjee, S., Degradation of dibenzodioxin during chlorine dioxide bleaching of kraft pulp. Environ. Sci. Technol. 1992; 26: 1324-1326.
9 Paasivirta, J., Organochlorines from pulp mills and other sources. Research methodology studies 1988-91, ed. Jaakko Paasivirta. Department of Chemistry, University of Jyväskylä, research report 1992; 38: 25.

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