

Effects of Sulphur/Chlorine Ratio and Limestone on PCDD/F Formation from Combustion of Waste Plastic Materials in Fluidized Bed Steam Boiler

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One way of utilizing waste plastic material is to recover its energy content. A proposed way is co-combustion, where waste plastic materials are burnt as a supplementary fuel in power or district heating plants. However, combustion of organic materials, especially in the presence of chlorine, is widely recognized as a source of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). In this investigation, the possibility to use sulphur containing coal to inhibit the formation of chlorinated hydrocarbons like PCBs and PCDD/Fs was studied when waste plastic materials were used as a supplementary fuel in a bubbling fluidized bed steam boiler. It has been suggested that increased S/Cl ratio would decrease the formation of PCDD/Fs (Griffin 1986). The main aim of this investigation was to study the influences of limestone addition and the S/Cl ratio, relative to chlorine content in fuel, on the PCB and PCDD/F emissions.

INCENERATION TESTS

The tests were carried out in a 7 MW bubbling fluidized bed steam boiler. Coal, limestone and sand were fed via the screw conveyer above the bed. Waste plastic material was injected into the bed pneumatically through a cooled lance. The feeders for coal, limestone and plastic material were calibrated by weighing.

The waste plastic material feed was a synthetic mixture containing packing industry scrap. The mixture contained the following components; 60% polyethylene (PE), 20% polypropylene (PP), 15% polystyrene (PS), and 5% polyvinyl chloride (PVC).

During these tests the operation parameters were adjusted to ensure that primary air and temperature could be kept constant (O₂ content 10 %, dry gas, water addition to bed). The sampling of chlorinated organic compounds was isokinetic and was performed at one point in the sampling plane after the electrostatic precipitator (ESP). Sampling for flue gas emissions of chlorinated organic compounds employed a dust filter, condensate trap, and XAD adsorption resin. Dust samples were analyzed separately (particle fraction), but the condensate

and resin samples were combined and given as gas fraction.

The ESP consists of two parts, but more than 90% of the fly ash was captured from the first part (ESP1). The fly ash samples used in this investigation were collected from ESP1. PCDD/F analysis of the separated, purified fractions were performed with a high resolution mass spectrometry (VG 70 SE, resolution 10000). The tests were as follows:

A1 = coal 420 kg/h

B1 = coal 360 kg/h + plastics 40 kg/h

C1 = coal 230 kg/h + plastics 130 kg/h

D1 = coal 170 kg/h + plastics 180 kg/h

E1 = plastics 300 kg/h

E2 = plastics 320 kg/h + limestone 26 kg/h

D2 = coal 170 kg/h + plastics 180 kg/h + limestone 26 kg/h

B2 = coal 370 kg/h + plastics 40 kg/h + limestone 26 kg/h

A2 = coal 400 kg/h + limestone 26 kg/h

RESULTS AND DISCUSSION

PCDD/F samples were taken simultaneously from flue gas before and after ESP during the test D2. The sum of different PCDD/F concentrations in the total dust fraction before and after the ESP were 29.71 ng/Nm³ and 0.53 ng/Nm³, respectively. This indicates higher than 98% ash removal in the ESP. The degree of chlorination of the congeners passing through the ESP was observed to increase, especially in the gas fraction the amount of heptachloro- and octachloro dioxin and furan concentrations increased 400 and 700 %, respectively. Using the measured value of the collection efficiency of ESP, the estimated values of PCDD/F concentrations at the sampling site before ESP could be calculated. Figure 1 shows the estimated PCDD/F values before the ESP. The high level of PCDD/Fs in test E1 corresponds to the incomplete combustion as showed the increased CO concentration in flue gas.

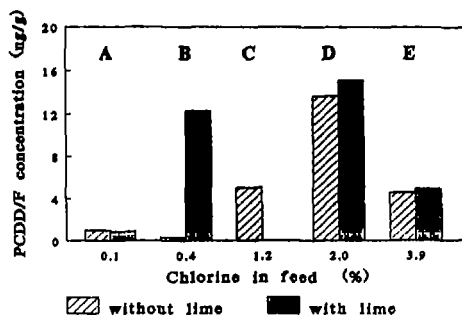
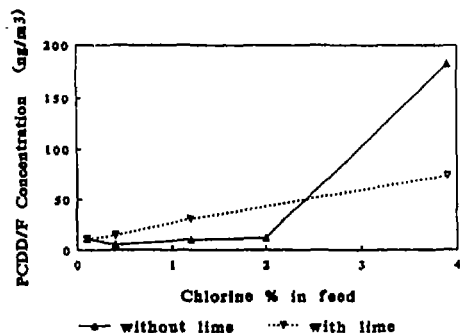


Figure 1. Estimated PCDD/F values before ESP. Figure 2. PCDD/PCDF concentration in fly ash.

The furans to dioxins ratio in the flue gas was 1.9 (range 0.9–2.9) for the tests without the addition of limestone and 2.7 (range 1.6–3.7) with the addition of limestone. The furans to dioxins ratio in fly ash was 0.17 (range 0.04–0.25) and 0.61 (range 0.26–1.5) without and with the addition of limestone, respectively. Addition of limestone was responsible for the increased PCDF values. This was clearly seen in both flue gas and fly ash samples. The ratio of PCDD to PCDF concentrations between gas and particle phases with low chlorine contents and with limestone was higher than without limestone, but with high chlorine contents the ratio was reverse. The PCDD/F concentrations in the fly ash samples are shown in Figure 2.

The PCDD/F compounds were mainly in the particle fraction of the flue gas. When considering the effect of S/Cl ratio on the PCB and PCDD/F concentrations, the better correlation was achieved before than after the ESP. The estimated results of the PCDD/F concentration are presented in Figure 3. The results showed that PCDD/F concentrations decreased linearly with increasing S/Cl ratio.

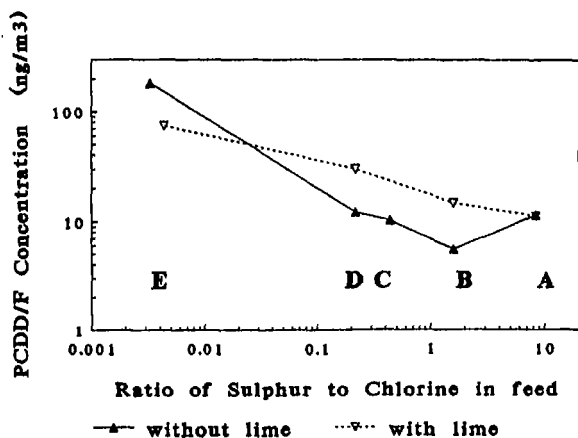


Figure 3. Estimated PCDD/F values for the sampling site before the ESP as a function of S/Cl ratio.

Because the particle concentration in the flue gas, and thus, in the total emissions of PCDD/Fs largely depended on the collection efficiency of the ESP, the linear multivariate regression analysis was only applied to the gaseous emissions and fly ash to study the regression between different parameters and PCDD/F concentrations. The correlations are shown in Table 1. The amounts of PCDD/Fs were highly dependent on CO in the flue gas. The coefficients in the Table 1 show that both the PCDD and PCDF concentrations in the flue gas decreased when the temperature in the upper part of the freeboard increased, and when the SO₂ concentration increased. HCl and CO had an opposite influence. According to the regression analysis, sulphur could have an inhibiting effect on PCDD/F formation. These results are in good agreement with the previously results of Geiger et al. (1992).

TABLE 1. Correlations of the total sums of PCDD/PCDF congeners to some parameters.

	Con- stant	HCl in gas	SO ₂ in gas	T freeb.	CO in gas	r ²
(in ash) PCDD	negat.	posit.	posit.	posit.	negat.	0.62
PCDF	posit.	posit.	negat.	negat.	posit.	0.91
(in gas) PCDD	posit.	posit.	negat.	negat.	posit.	0.90
PCDF	posit.	posit.	negat.	negat.	posit.	0.87

PCB compounds were saturated in the particle/ash fractions. Regression analysis gave a satisfactory result with CO, O₂ and S/Cl ratio in the flue gas. When the S/Cl ratio in the flue gas decreased, PCB concentration in both flue gas and ash increased. The correlations are shown in Table 2.

TABLE 2. Correlations of the total sums of PCB congeners to some parameters.

	Con- stant	T freeb.	CO in gas	O ₂ in gas	S/Cl in gas	r ²
PCB, gas	negat.	posit.	posit.	negat.	negat.	0.95
PCB, ash	negat.	posit.	negat.	posit.	negat.	0.94

SUMMARY

Results are reported from the co-combustion of coal with waste plastic material. The tests were performed in a bubbling fluidized bed steam boiler with and without limestone. The purpose of the tests were to examine the possibility to use coal containing 0.5% sulphur to inhibit the formation of chlorinated hydrocarbons like PCDD/PCDFs or PCBs by testing of the S/Cl ratio on the formation of these compounds in full scale experiments. The presence of high content of sulphur, relative to the level of chlorine in the fuel, seemed to decrease the formation of PCDD/Fs. Limestone addition slightly increased PCDD/F emissions.

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