

Pebble Heater suppresses Synthesis of Dioxins and Furans in Off-gas generated by Incineration of Halogen-rich Fuel from WEEE

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Introduction

Changes in German and European legislation have led to altered approaches for the disposal of polymer-rich shredding residues (SR). Whereas disposal in landfills was the strategy of choice in the last decades, thermal treatment is supported now. However, when waste electric and electronic equipment (WEEE) is the source of SR, thermal treatment is complicated by a) a bromine and chlorine load in the lower percent range ¹, b) the presence of polybrominated dioxins and furans (PBDD/F) in the ppb range ² and c) by brominated flame retardants including polybrominated biphenyl ethers, which serve as dioxin precursors ³.

Hence, SR-based fuels require a state-of-the-art incineration and a state-of-the-art exhaust cleaning, which reduce emissions of polychlorinated dioxins and furans (PCDD/F) below 0.1 ng I-TEQ/Nm³, as demanded by European directive 2000/76/EC ⁴. High temperature incineration with sufficient residence time is able to destroy more than 99% of PCDD/F present in the fuel, raw gas cooling, however, has to suppress a “post-combustion” synthesis of polyhalogenated dioxins and furans (PXDD/F) effectively ⁵. Post-combustion dioxin synthesis is mainly related to two mechanisms, a) the condensation of precursor molecules (mainly halogenated benzenes and phenols) which are present in the feed or might be formed during incineration of halogenated aromatic compounds and b) the *de-novo*-synthesis which is due to heterogeneous catalytic reactions of halogens with short chain organic compounds. As reviewed by McKay these both mechanisms are dominant in the temperature range between 250-450°C ⁵. Thus, especially with regard to halogen rich fuels, a very rapid gas cooling from 450° to 250°C is the main goal of raw gas treatment ⁵, which is normally realised by scrubbing with water ⁶.

The pebble heater technology developed by ATZ Evus (Sulzbach-Rosenberg, Germany) might serve an alternative to the state-of-the-art devices. It bases on the application of a pebble bed of natural bulk material, which the exhaust gases flows through radially. High flow velocities and/or smaller pebble diameters may be used, as there is no danger of fluidization. That provides a very high specific surface and consequently an excellent heat transfer. That results in a high thermal efficiency (units with more than 98% energy recovery are in operation) and a temperature gradient

in the range of 1500 – 2000 K/m⁷. Consequently, exhaust gases pass the temperature range of 450-250 °C within 50 milliseconds, approximately.

Here we present data of a pilot application of the pebble heater technology for the treatment of raw gas derived from the incineration of polymeric materials from WEEE. Since the pilot experiments were performed on an existing pebble heater test plant in the small-technical scale, waste throughput and experimental design had to be adjusted to the given circumstances. As the study focussed on exhaust treatment and not on the incineration process itself, a liquid fuel was applied as a model for SR from WEEE. The incineration of a liquid fuel was preferred, since it could be implemented in the given test plant by spray injection, thus minimising technical modifications of the test plant and optimising the combustion efficiency compared to incineration of solid polymer granulates.

Fuel and exhaust gases, which passed the pebble heater bed, were sampled and analysed for PCDD/F and PBDD/F. The pilot incineration was tested for the compliance with the PCDD/F emission limits given by European directive 2000/76/EC, and overall mass balances were calculated for PCDD/F and PBDD/F.

Methods and Materials

Fuel description

Fuel was derived from a small-technical scale extraction of a polymer fraction of WEEE with hexane. The extract contained PBDD/F, halogenated flame retardants and styrene and PVC polymers. Hexane was evaporated and the residue was dissolved in a low amount of a high boiling solvent (CreaSolv-PSTM, CreaCycle, Grevenbroich, Germany). This viscous solution was fortified with virgin styrene polymers to adjust a viscosity of approximately 40 mPas (at 23°C).

Fuel analysis

Fuel was analysed for halogens by x-ray fluorescence spectrometry (EDXRF). Bromine and chlorine were quantified using calibration standards prepared with polymer solutions. Flame retardants were analysed by HPLC-UV/MS. Details of the method are described elsewhere⁸. After addition of ¹³C-labelled internal standards PBDD/F and PCDD/F were analysed by soxhlet extraction, a multi-step column clean-up including acid/basic silica, alumina and florisil, and GC-HRMS (MAT 90, Finnigan). Details of the method were described by Ebert et al.⁹.

Incineration experiment

The experimental design of the fuel incineration and exhaust treatment is depicted in figure 1. Before fuel incineration, the gas flow direction was switched between back-flush and incineration mode several times, using natural gas to run both, ignition and main burner. This allowed to heat the fuel ignition zone, located above the combustion chamber, and to create and to maintain a steep temperature gradient in the pebble heater bed.

During the incineration experiment, the switching between both modes was continued. In the forward incineration mode, fuel was sprayed into the preheated pipe with a mean flow rate of approximately 8.1 kg/h. Combustion gases were transferred into the combustion chamber with 100 Nm³/h and burned with temperatures between 800 and 1100°C. Subsequently, they were cooled in the pebble heater bed achieving a temperature below 200°C at the cold grid.

After ten minutes, fuel injection and natural gas incineration were stopped, the device switched into the backflush mode and the temperature gradient in the pebble bed was regenerated. In this mode, hot gases maintain temperatures in the ignition zone which are approximately 100°C lower than combustion temperature and exit the upper side of the test plant, where they might be used for energy recovery or steam generation. When the steep temperature gradient is regenerated, the system was switched into forward direction and fuel injection as well as natural gas incineration continued.

However, the switching mode and thus the discontinuous incineration is related the test plant concept. Up-scaled pebble heaters can be run continuously, either by application of two pebble heaters in tandem processing or by a spatial separation of forward and back-flush mode in one pebble heater device.

Emission sampling and analysis

In accordance to European norm EN 1948 part 1, emission sampling was performed directly after the cold grid with the cooled probe method, applying PU foams as adsorbent. The analysis of emission samples based on European norm EN 1948 parts 2 and 3 using ¹³C-labelled internal standards for both, PCDD/F and PBDD/F.

International toxicity equivalents (I-TEQ) were calculated for PCDD/F using the NATO I-TEQ scheme. PBDD/F-I-TEQ were estimated using the concentrations of 2,3,7,8-brominated tetra-to penta-brominated furans and tetra- to hexa-brominated dioxins as well as the toxicity equivalent factors (TEF) of their chlorinated analogues.

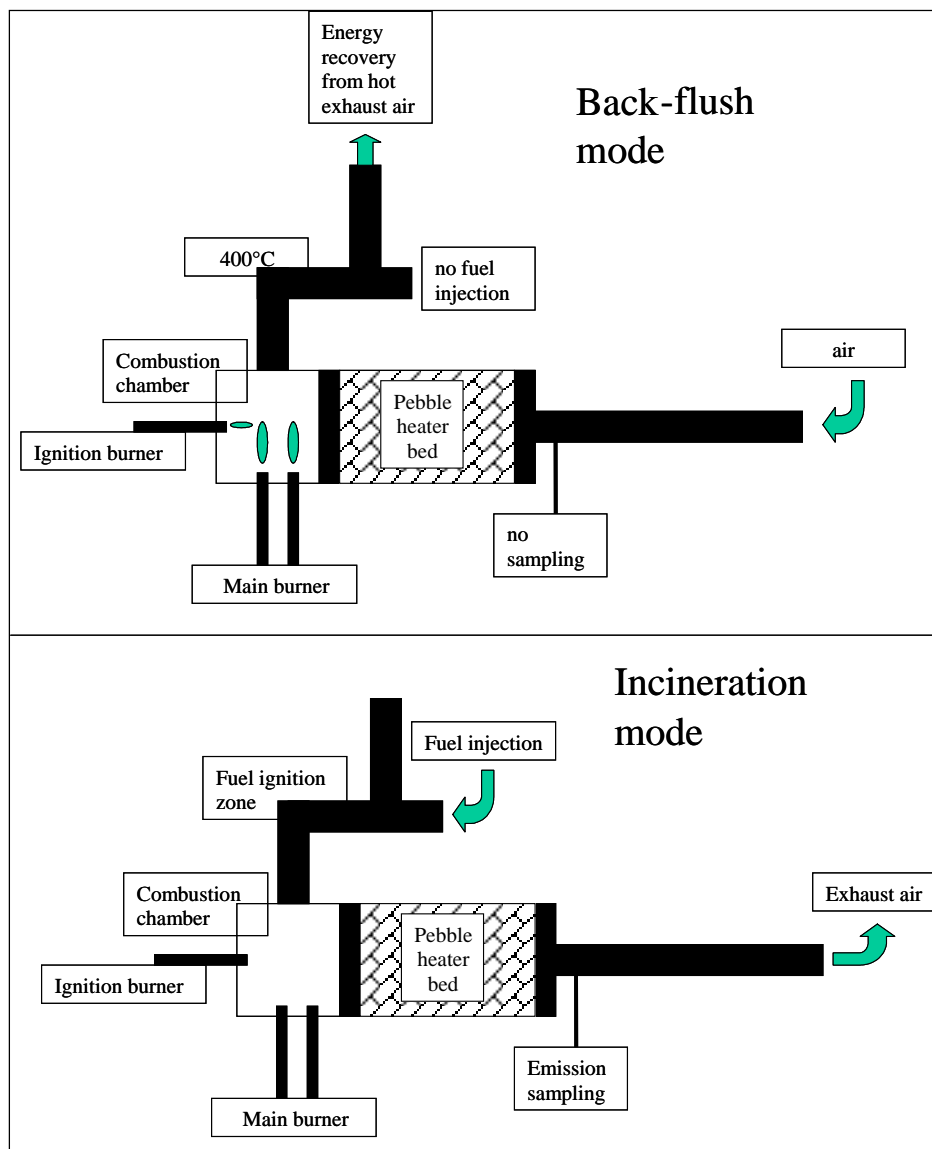


Fig. 1: Experimental design of the pilot incineration of halogen-rich fuel and exhaust cleaning by the pebble heater technology.

Results and Discussion

Table 1 displays the results of the analytic fuel characterisation. Halogen concentrations are in the typical range of SR fractions^{1,10}. Four brominated flame retardants were identified with concentrations between 1730 and 6130 ppm. PBDD/F levels were above the thresholds of the German Chemikalienverbotsverordnung¹¹, PCDD/F concentrations accounted for 14 pg I-TEQ/g. Thus with regard to halogens and polybrominated compounds, the fuel reflects typical SLF from

WEEE, as we learned in a different study. However, the polymer content of the fuel is reduced to one third compared to real SR by the dissolution approach. Since the solvent applied and the polymers expected in WEEE are characterised by comparable elemental composition, the liquid fuel is considered an appropriate model for SR from WEEE.

Table 1: Results of fuel analysis

| | |
|---|------|
| Chlorine, % | 0,68 |
| Bromine, % | 1,20 |
| Octabromodiphenyl ether, ppm | 5300 |
| Decabromodiphenyl ether, ppm | 1730 |
| 1,2-bis-Tibromophenoxyethane, ppm | 5500 |
| Tetrabromobisphenol A, ppm | 6130 |
| PBDD/F ^{a,c} , Sum 4 according to ChemVV, ng/g | 4.21 |
| PBDD/F ^{b,c} , Sum 5 according to ChemVV, ng/g | 9.44 |
| PCDD/F pg I-TEQ/g | 14 |

^a: Sum 4 encloses 2,3,7,8 TeBDF, 2,3,7,8-TeBDD, 2,3,4,7,8-PeBDF, 1,2,3,7,8-PeBDD

^b: Sum 5 includes sum 4 plus 1,2,3,7,8-PeBDF and all three 2,3,7,8-brominated HxBDD isomers

^c: Threshold values for sum 4 and 5 are set to 1 and 5 ng/g, respectively ¹¹.

We had to experience that the lack of an exact fuel dosage in our incineration experiment caused fuel residence times below 1 second temporarily, which is less than expected to be sufficient for a complete incineration⁵. Consequently, products of incomplete combustion, CO and black smoke, were identified in the emission samples and in the off-gas.

Nevertheless, elimination rates between 76-99% were obtained for PBDD/F (see fig. 2), which is in agreement with elimination rates reported for incineration of SR from WEEE by Sikh¹ or Vehlow and co-workers¹⁰, especially when taking into account, that no dust filters were applied. The mass balance of PCDD/F (table 2) reveals a significant elimination instead of a post combustion synthesis, regardless the high chlorine load of the fuel and the incomplete combustion. Consequently, elimination rates below 95%, as calculated for 2,3,7,8 TeBDF and 1,2,3,7,8-PeBDD, are considered to be due to incomplete combustion and not to be a result of a post combustion synthesis.

Table 2: PCDD/F-Elimination rates

| ng I-TEQ PCDD/F in fuel | ng I-TEQ PCDD/F in exhaust gas | Elimination rate |
|----------------------------|-----------------------------------|------------------|
| 132 | 4,6 | 96 % |

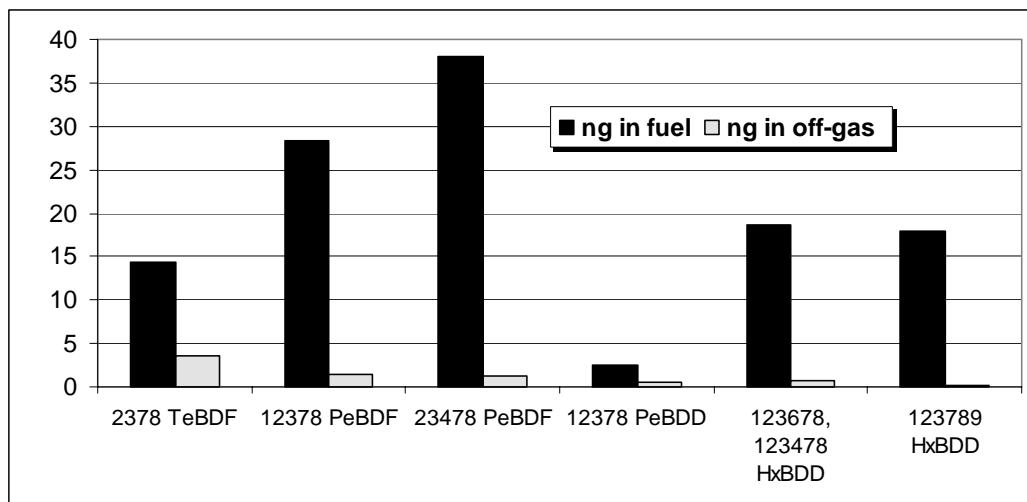


Figure 2: Elimination of PBDD/F by incineration and exhaust cleaning based on the pebble heater technology.

Emission values in terms of I-TEQ are listed in table 3. With regard to PCDD/F the emission is in compliance with the strict European level of 0.1 ng I-TEQ/Nm³ ⁴. Thus, the pebble heater has proved to be sufficient in suppressing a synthesis of PCDD/F.

Table 3: Levels of PCDD/F and PBDD/F obtained in the emission samples

| | ng I-TEQ/Nm ³ in exhaust | Threshold limit (ng I-TEQ/Nm ³) |
|---------|-------------------------------------|---|
| PCDD/F | 0.04 | 0.1 |
| PBDD/F* | 12.3 | Does not exist |

* I-TEQ for PBDD/F based on the concentrations of eight 2,3,7,8-brominated PBDD/F and the TEF of their chlorinated analogues.

However, calculating a PBDD/F-based I-TEQ value, the emissions account for 12.3 ng PBDD/F-I-TEQ/Nm³. Since PBDD/F and PCDD/F exhibit comparable toxicities on a molar level as stated by Weber and Greim it is reasonable to add more than 50% of the PBDD/F-I-TEQ to the measured PCDD/F-I-TEQ emission ¹². This approach would result in the emission levels exceeding the limit of 0.1 Nm³ by far. If 2,3,7,8-substituted mixed halogenated dioxins and furans were included additionally, a further increase of the emission levels would be expected. Nevertheless, at present there are no restrictions for the emission of brominated and mixed-halogenated 2,3,7,8-substituted dioxins and furans.

Our data point out, that thermal treatment of SR from WEEE, which is characterised by high levels of PBDD/F and negligible PCDD/F concentrations, requires both, a complete combustion process and an adequate exhaust treatment. However, if only the first process is disturbed, which might happen in real incineration plants also, incomplete combustion will lead to increased PBDD/F emissions without increasing PCDD/F emission limits.

Thus, monitoring of PCDD/F emissions only is not sensible to reveal improper thermal waste treatment and therefore an ineffective means for assessing resulting health risks. Consequently, the implementation of PBDD/F emission limits into existing emission directives is recommended urgently, at least for those waste treatment plants, which are considered to handle the increasing amounts of PBDD/F-containing polymers from WEEE in future.

However, since the insufficient elimination of TeBDF and PeBDD observed in our pilot experiment was related to incomplete combustion and not to the pebble heater approach, further application tests of this exhaust gas treatment approach are planned with an improved incineration technology.

Acknowledgements

We thank the Bavarian Ministry of Economic Affairs, Infrastructure, Transport and Technology for their financial support.

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