Investigations on thermic inertisation of MWI-residues

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1. Introduction

Since the detection of polychlorinated Dibenzo-p-dioxins and Dibenzofurans in emissions of waste incinerators in 1977 they are in the criticism of the public eye. In Germany the total amount of PCDD/F-emissions of waste incinerators has been estimated as about 360 - 630 g TE-Int. in 1990 [1]. Since the Ordinance on Incineration Plants for Wastes was put into force in 1990, a limit value for dioxins in the exhaust gases to 0.1 ng/Nm^3 I-TE is valid. Therefore the dioxins amount in stack gases from MWIs will decrease to about 5 g I-TE per year.

With this step the disposal and commercial use of the rest substances, especially fly ashes, becomes more and more important.

For that reason the Bavarian Department of Environmental Protection has made vitrify reactions with fly ash, reaction products from fluegas cleaning, washer-residues and slag of MWIs.

2. Experimental

a) Thermic inertisation of fly ashes, washer-residues and slags in a chamber oven (T = 1500°C, 10 min)
About 20 g MWI-residue were weighed in an alinit-box. The sample was given in a chamber oven and then heated with 10°C/50 s to 1500°C. After 10 min at this temperature the oven was cooled. The residue was cleaned up like described in 2).

b) Thermic inertisation of fly ashes in a tube-oven
About 1 g of the fly ash was weighed in a quartz box and given in a quartz-tube in the oven. The sample has been pyrolysed at 1.100°C about 45 min under air (200 ml/min). The flue gas was adsorbed in an impinger with toluene followed by an XAD2-resin. The sample residue as well as the toluene of the impinger and the XAD-2 have been analyzed for PCDD/F 2).

c) GC/MS-analysis

The GC/MS-analysis was made with a high resolution mass spectrometer Autospec and a GC Hewlett Packard 5890.

Temperature program:	100°C, 3 min isotherm, Rate 1: 20°/min to 180°C; Rate 2: 5°/min to 250°C; 50 min isotherm
Injector:	KAS 3, splitless
Carrier gas:	Helium
Capillary column:	SP 2331, 60 m, 0,32 id., film thickness 0,2 µm

The HRGC/HRMS-analyses has been made in SIM-mode.

3. Results

a) Thermic inertisation in a chamber-oven at 1500°C

Sample	Initial product I-TE (ng/kg)	Pyrolysis product I-TE (ng/kg)
Tissue filter residue *) MWI-G	967.7	< 0.29
Electrostatic precipitator ash MWI-L	3 957.1	0.21
Washer-residue MWI-L	2 698.1	0.25
Tissue filter Mixture of restproducts MWI-R	2 905.7	0.29
Tissue filter residue *) MWI-Nü	2 399.1	< 0.29
Tissue filter residue *) MWI-K	898.3	< 0.29
slag MWI-B	14.1	0.24
Tissue filter residue *) MWI-Ne	871.7	0.35
Tissue filter residue *) MWI M-Süd	340.0	0.29

b) Thermic inertisation in a tube oven (T = 1100°C, air 200 ml/min)

Sample	Initial product I-TE (pg)	Residue I-TE (pg)	Emission I-TE (pg)
Electrostatic precipitator ash MWI-L	4 075.8	4.2	1 805.0
Tissue filter residue *) MWI-G	822.5	15.7	9.1
Tissue filter residue *) MWI-Ne	871.7	6.2	4.0

*) reaction products from fluegas cleaning

4. Discussion

The literature [3-8] show some processes for thermic inertisation of MWI-residues. Investigations from EMPA with the electrical melting process [3] for destruction of PCDD/F in MWI-residues, in the residues have been detected the following PCDD/F-concentrations:

Table: Concentrations of PCDD/F in fly ash "glass" and concentrate

ng/g (ppb)	fly ash	"glass"	metal concentrate
Tetra CDD	1.3	<0.04	<0.06
Penta CDD	2.5	<0.02	<0.01
Hexa CDD	11	<0.08	<0.02
Hepta CDD	40	0.08	<0.015
Octa CDD	90	0.15	<0.06

Other authors show [5,7,8] that all organic substances are destroyed completely, thus also dioxins and furans.

a) Thermic inertisation of fly ashes, washer-residues and slags in a chamber-oven
The results show that the relation of PCDD/F-concentration of the pyrolysis products and the original product is about between 2×10^{-2} and 1×10^{-4} TE-Int. The PCDD/F-concentrations of the pyrolysis products all are below 30 ppt TE-Int. and in the same amount as shown in studies of Jochum et al [3]. This concentrations are even below the PCDD/F-contents of soils.

b) Thermic inertisation of fly ashes in a tube-oven
The results show that the PCDD/F-concentrations in the residues from MWI-G and MWI-Ne are reduced considerably. In the pyrolyses residue only 0.7 % respectively 1.9 % of the PCDD/F were found again. In the stack gas the concentrations are similar. Different from this is a fly ash from the MWI-L

where in the stack gas high PCDD/F-concentrations were found (44.3 %), in the residue the concentration was like in the others.
Possible reasons for this phenomena could be, that the PCDD/F in the different MWI residues exist in different forms of adsorption and/or in the melts from Tissue-filter residues, with an higher amount of calciumoxide and therefore an higher alkalinity, the dioxins/furans are widely destroyed by dechlorination reactions. To get more informations about these problems more investigations are necessary and are planed within a larger project beginning in may 1995.

References:

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