HAGENMAIER DRUM - FLY ASH DECHLORINATION/ HYDROGENATION PROCESS: COMBINATORIAL BIO/CHEMICAL ANALYSIS

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Introduction

Low temperature treatment (below 400 °C) of fly ashes under oxygen deficiency conditions (thermo-catalytic treatment or Hagenmaier process) has been already applied on several municipal waste incinerator plants in Germany[1,2,3,4] and Japan[5,6] as a successful method for the reduction of dioxins and related compounds.

Hagenmaier (1988)[1] obtained reductions of PCDD/Fs in a range of 95 to 99.9%, and for PCBs, chlorobenzenes and chloronaphthalenes of 93%. Also Ishida et al. (1996)[5] reported about a decrease in the I-TEQ from 0.6 I-TEQ ng/g in untreated ash to 0.002 I-TEQ ng/g (99.7% PCDD/Fs decompostion ratio) in treated ash (350° C, 1 h retention time). In addition, Sakai (1999)[5] also showed that TEQ-values from about 100 µg TEQ/ton waste on average (combustion technologies in 1999) could be reduced to about 3.8 µg TEQ/ton waste on average (96% treatment efficiency). This result is comparable to the also in the same study reported 4.15 µg TEQ/ton waste on average gasification melting technology. The future target in Japan for the total amount of PCDD/Fs released by regulatory standards is 5 µg TEQ/ton waste on average[6].

The aim of the present study was to confirm the decrease of PCDD/F-TEQs, bioassay-TEQ-values (measured by Micro-EROD[7-11] and DR-CALUX®-bioassays[12,13]) and therefore the total sum of dioxin-like activity for two fly ashes treated by the Hagenmaier process in one incineration plant.

Materials and Methods

1. Fly ash dechlorination/hydrogenation treatment

Fly ash from a fabric filter and a gas cooling tower is fed into the Hagenmaier drum for thermal dechlorination of PCDD/Fs, and afterwards treated for stabilizing heavy metals by chelate resin. The dechlorination process consists of a reactor (Hagenmaier drum) and a cooler as main equipment. Fly ash is charged into the reactor through the inlet rotary valve, heated up (at least 350° C) under exclusion of air (O_2 < 1 %; done by introducing N_2 gas). The best decontamination results were obtained in the temperature range of 350-400° C and residence time for the ash of at least 30 min.

2. Fly ash sampling, clean-up and analysis

Sampling (12.5-25 g untreated fly ash and 50 g treated fly ash), clean up (without oxidative clean-up) and analysis of PCDD/Fs in treated and untreated fly ash were carried out according to previous publications[8,9].

3. DR-CALUX®- and Micro-EROD-bioassay

a.) DR-CALUX®-bioassay (BioDetection Systems, BDS): The validation samples and treated/untreated fly ash samples were analysed according to the guidelines from BDS (www.biodetectionsystems.com) and recently published studies[12,13].

b.) DR-CALUX®-bioassay (Kaneka Corporation, KC): The samples at KC were also analysed according to a.), but the luciferase activity was measured using LucLite™ (Packard) and the TopCount NXT® Microplate Scintillation & Luminescence Counter (Packard).

c.) The Micro-EROD bioassay was performed as already published[11].

Results and Discussion

As cross-validation study for the DR-CALUX® technology, three fly ash samples (a/b/c; in ng TEQ/g) and one emission gas (d; in ng TEQ/m^3) were analysed at BDS and KC. These samples were additional analysed by chemical analysis and Micro-EROD bioassay {a/b/c/d in brackets}:

- DR-CALUX®-TEQ {at BDS: ashes: a=237/b=130/c=13.8/emission gas d= 97};
- DR-CALUX®-TEQ {at KC: 209/134/16.5/72};
- Micro-EROD bioassay {analysed at KC: -/51/5.1/8.9} and TEQ {chemical analysis at BDS or KC: 95/43/5.3/8.7}.

The resulted DR-CALUX® TEQ values for both laboratories were comparable.

After the cross-validation study with BDS, two untreated and four treated fly ashes (Hagenmaier process) were analysed at KC (see Table 1):

- The TEQ/EROD-TEQ/DR-CALUX®-TEQ values of the untreated fly ash No. 1 could be decreased from 12/18/59 ng TEQ/g to finally 0.11/0.14/- ng TEQ/g for treatment No. 1a and to 0.0018/0.0033/0.021 for treatment Nr. 1b.
- Fly ash No. 2 could be efficiently reduced from 2.1 (TEQ)/3.9 (EROD-TEQ)/2.6 (DR-CALUX®-TEQ) ng/g to finally 0.11/0.42/0.15 (Treatment No. 2a) and 0.017/0.022/0.021 (Treatment No. 2b).
- This resulted in a treatment efficiency for these fly ashes from 95-100 % in TEQs; 94-100% in DR-CALUX®-TEQs and 89-100% in EROD-TEQs.
- The Ratio between bioassay-derived TEQ and TEQ values for untreated fly ash (Micro-EROD: 1.5/1.9 and DR-CALUX®: 4.9/1.2) and treated fly ashes (Micro-EROD: 1.3; 1.8/3.8; 1.3 and DR-CALUX®: -; 12/1.4; 1.2) were similar to previously reported studies[7-10].

Dose-response curves of the DR-CALUX® activity are shown in Graph 1 (24 h kinetic; curves were fitted using a one-ligand curve-fit; three independant measurements; EROD dose-response curves were similar).

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Graph 1: Dose-response curves of DR-CALUX® activity from untreated (n=2) and treated (n=4) fly ash samples (by the Hagenmaier process).

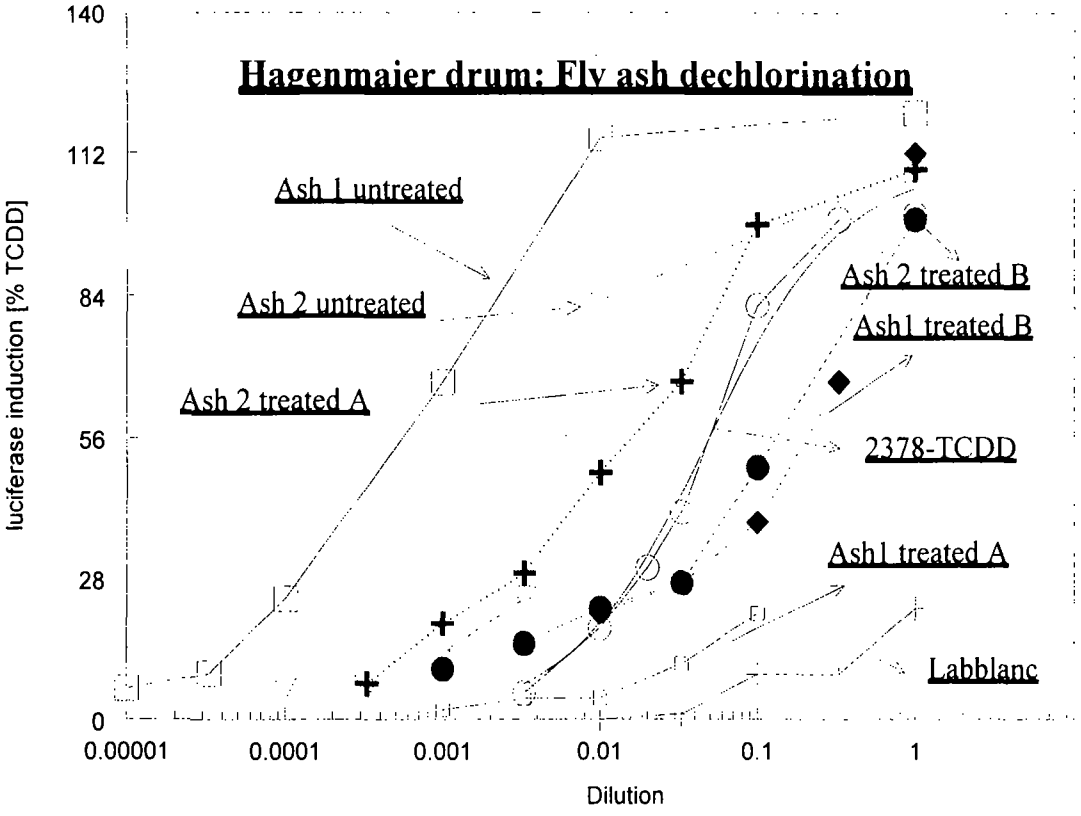

Table 1 : DR-CALUX®- -T [b] and T (PCDD/Fs)- values for treated and untreated fly ashes (Hagenmaier process) {ng T /g}
[n number of measurements; SD standard deviation; CV coefficient of variation (%)]

Sample	CALUX-T ®	ROD-T	T	CALUX-T ®/T	ROD-T /T
Sample 1					
Untreated 1	**59** [3;8;14]	**18** [5;5;28]	**12**	4.9	1.5
Treated 1a		**0.14** [5;0.06;41]	**0.11**		1.3
Treated 1b	**0.021** [4;0.003;16]	**0.0033** [5;0.0033;25]	**0.0018**	12	1.8
Treatment efficiency [%]	99.96	100	99.1-100		
Sample 2					
Untreated 2	**2.6** [6;0.63;24]	**3.9** [5;0.47;12]	**2.1**	1.2	1.9
Treated 2a	**0.15** [4;0.17;20]	**0.42** [5;0.2;47]	**0.11**	1.4	3.8
Treated 2b	**0.021** [3;0.0005;2]	**0.022** [5;0.022;25]	**0.017**	1.2	1.3
Treatment efficiency [%]	94.2-99.2	89.2-99.4	94.8-99.2		

[a] The procedure blank (13.8 pg abs.; n=3). was at least 80-times lower lower than the lowest T value. The DMSO blank was substracted.
[b] The procedure blank (9.3 pg abs.; n=2). was at least 10-times lower lower than the lowest T value. The DMSO blank was substracted.