DIOXIN DESTRUCTION EFFICIENCY OF CATALYTIC FILTERS - EVALUATION IN LABORATORY AND COMPARISON TO FIELD OPERATION

Roland Weber[1], Marc Plinke[2], and Zhengtian Xu[2]

[1] Environmental Process Development Department, Ishikawajima-Harima Heavy Industries Co., Ltd.,1, Shin-Nakahara-cho, Isogo-ku, Yokohama 235, Japan
[2] W. L. Gore & Associates, Inc., 101 Lewisville Road, Elkton, MD 21921, USA

Introduction

Aim

The first goal of this study was to find a lab test method for dioxin destruction where the results would correlate to field measurements. The second goal was the evaluation of the gas phase dioxin destruction potential of the REMEDIA™ PCDD/F catalytic filter system. Dioxin destruction measurements in the lab were compared with six (6) field measurements. The PCDD, PCDF and TEQ values were compared and showed a high degree of similarity, validating the lab test method.

Additional tests of the REMEDIA D/F catalytic filters showed a destruction efficiency in excess of 99.9% with inlet concentrations of up to 100,000 ng/Nm^3. Such a lab method would help plant operators and legislature authorities to assess the performance of the new catalyst filters.

Background

Dioxins are emitted in trace amounts from municipal and medical waste incinerators. Emission values for PCDD/F of 0.1 ng I-TEQ/Nm^3 for municipal and hazardous waste incinerators have been in effect in several European countries and for new municipal waste incinerators (MWIs) in Japan[1-3]. At present, primary measures such as design and operation of the firing system to minimize the formation of "products of incomplete combustion" (combustion technology) or boiler technology (i.e., influencing of the *de novo* synthesis in the cooling of flue gas) cannot guarantee compliance with the stringent emission value[4].

The catalytic destruction of the PCDD/F in the flue gas[5,6] is a proven technology to enable stack gas values below 0.1 ng I-TEQ/Nm^3. It was demonstrated recently that catalytic filter systems also have the potential to destroy dioxin/furans below the regulation limit of 0.1 ng/Nm^3 I-TEQ[7]. It has already been shown during the catalytic filter's three-year performance in MWI plants that the long-term catalytic activity did not decrease, thereby promising the full lifetime expectation of the filter bag material of five (5) or more years.

Materials and Methods

Catalytic Filtration Product Information

The REMEDIA™ catalytic filter system is manufactured by W. L. Gore & Associates, Inc. (Gore) and is described elsewhere[7].

Laboratory Experiments

The catalytic felts were tested in a stainless steel reactor at 200°C. The volumetric flow through the catalyst felt of 300 cm^3/min (20% O_2, 80% N_2) corresponds to a flow velocity of about 1 m/min through the catalytic filter and is, therefore, comparable to the actual flow in MWIs through the filter bag.

Removal efficiency (RE) describes the ability of the filter to remove dioxins from the gas stream (Figures 1 to 3). It is calculated as (PCDDin – PCDDout)/PCDDin. DE (destruction efficiency) describes the ability of the filter to destroy dioxins during the experimental time of one hour. It is calculated as (PCDDin – [PCDDout + PCDDon cat])/PCDDin.
The catalysts are extracted by 12 hours Soxleth extraction. The catalyst and impinger are analyzed separately for PCDD/F. Clean up and analysis are described elsewhere[8].

Results and discussion

Destruction Removal Efficiency of Fresh Catalytic Felt
In a first measurement series, fresh catalytic filter samples were tested for their PCDD/F removal efficiency at 200°C. In all four measurements the catalyst showed high removal efficiency (RE) for PCDD and PCDF (Figure 1). The total RE for tetra- to octachlorinated dibenzo-p-dioxins and dibenzofurans lay above 99%, and the total TEQ decreased in average to more than 99.6% (Figure 1). The PCDDs were removed with a slightly higher efficiency than the PCDF. The same trends can be observed in actual municipal waste incinerators and the RE in laboratory and field are in good agreement (Figure 1).
That the high removal efficiency indeed results from destruction and not from an adsorption phenomena became obvious when analyzing the catalyst. After a one-hour experiment, only 0.05% of TEQ was detected on the catalytic felt. This is in agreement with the detection of only trace amounts of Dioxin on the catalyst felt after 2 years of operation in a MWI. Considering the PCDD/F not removed by the filter and the amount of PCDD/F on the catalyst, the average destruction efficiency of total PCDD/F was higher than 99% and of I-TEQ, higher than 99.5%.

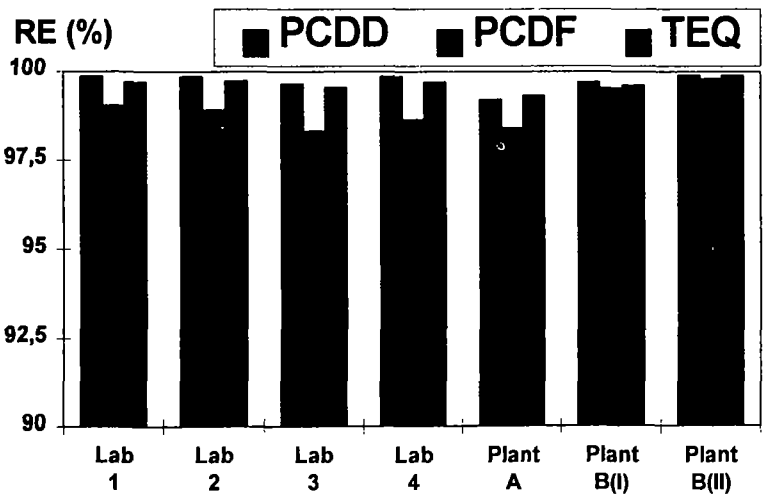

Figure 1: Reproducibility of the removal efficiency (RE) of a fresh catalyst felt in laboratory test and comparison to field operation in municipal waste incineration.

When comparing the congeners on the felt (Figure 2), no lower chlorinated isomers (T_4CDD/F and P_5CDD) were detected on the catalyst, as most of them were destroyed. For H_6CDD already more than 99.9% were destroyed. in comparison to 99.65% for H_6CDF. For the perchlorinated OCDD 99.62% were oxidized in comparison to 98% of the OCDF. Therefore, the destruction rate increases with decreasing degrees of chlorination and the destruction rates for PCDD on this catalyst are somewhat higher compared to PCDF. The same destruction behaviour we observed in the catalytic study with another honeycomb type catalyst[9]. This result explains the somewhat higher RE for PCDD in the laboratory test and plant operation compared to PCDF (see above).

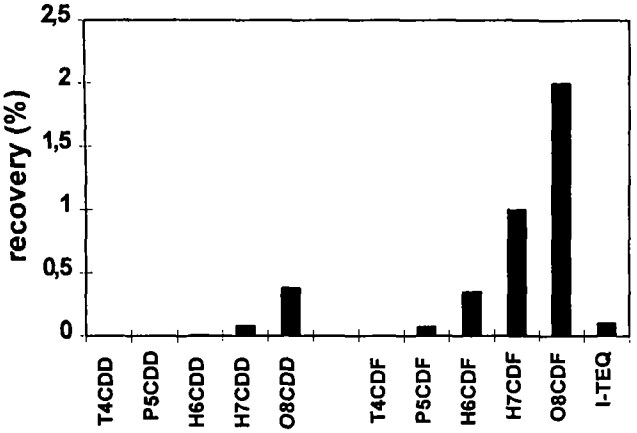

Figure 2: Recovery of PCDD and PCDF adsorbed on the catalytic felt in the laboratory test at 200°C.

What are remarkable are the concentrations that the catalytic filter was able to remove in the laboratory experiments. In the laboratory, a much higher amount of PCDD/F concentration/felt surface was used compared to values in the MWIs. Raw gas values of PCDD/F in the MWIs are typically around 3-30ng TEQ/Nm^3, corresponding to about 200-4000 ng/Nm^3 total PCDD/F. In the laboratory experiments, a total of 410 ng T_4CDD/F-OCDD/F was used corresponding to more than 100,000 ng/Nm^3 total PCDD/F during the evaporation phase. These results suggest that the catalytic filter should destroy PCDD/F even in incinerators with highest PCDD/F levels with more than 99% efficiency.

Comparison of Felts with Different Catalytic Activities in Field and Laboratory

In a second experimental series it was tested to see if the laboratory experiment could predict different activities of catalytic felts from the field. For this test three (3) catalytic filter samples (AA, BB, CC) were tested after exposure in a variety of plants.

Sample AA was from a municipal waste incinerator after two (2) years of operation. The two other samples (BB and CC) were deactivated during field operation under special circumstances in non-incineration plants during one-week tests.

The AA sample from the MWI shows a removal efficiency of more than 99% (Figure 3) and therefore, the same activity compared to the new catalytic felt B (Figure 1). The laboratory measurements produced the same results (Figure 3). The two-year exposure to waste incineration off gas did not decrease the activity of the catalyst nor change the physical property of the felt.

The partly deactivated sample BB showed low RE in the pilot plant operation (Figure 3). The RE in the laboratory test and the field measurement showed an amazing similarity (Figure 3). The PCDFs were removed in the laboratory to 74.6% and in the field to 69.5%. The RE measurements for PCDD were 95.2% in the field and 96.6% in the laboratory.

After poisoning in the field, catalyst sample CC showed no removal efficiency of PCDD/F in the field measurement (Figure 3). In the laboratory, a removal efficiency of 26.7% for PCDF and 51% for PCDD were assigned (Figure 3). However, the analysis of the PCDD/F on the felt proved that the "missing" amounts were adsorbed on the catalyst and not destroyed (Figure 3). While on the fresh catalyst under the same conditions, only a negligible amount remained (see above + Figure 2). Therefore, catalyst felt CC also showed no destruction of PCDD/F in the laboratory.

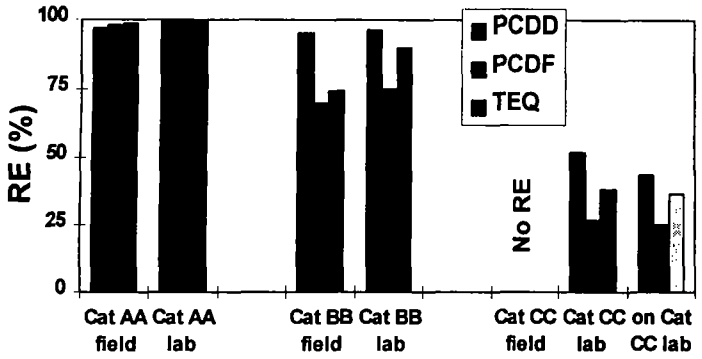

Figure 3: Comparison of removal efficiency of used catalytic felts from MWIs (AA) in laboratory and field, and after deactivation during field operation under special circumstances in non-incineration plants and laboratory testing (BB and CC) in one-week tests.

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