

Laboratory Test of SCR Catalysts Regarding the Destruction Efficiency towards Aromatic and Chlorinated Aromatic Hydrocarbons

Takeshi Sakurai and Roland Weber

Research Institute, Ishikawajima-harima Heavy Industries Co.,Ltd., 1, Shin-Nakahara-cho, Isogo-ku, Yokohama 235, Japan

Introduction

The stringent limiting value for PCDD/PCDF emission of 0.1 ng I-TEQ/Nm³ has been in effect in Japan since January 1997 for all new waste incinerators [1,2].

To ensure adherence to this limit value, the primary measures such as design and operation of the firing system to minimize the "products of incomplete combustion" (combustion technology) or the boiler technology, (i. e. influencing of the *de novo* synthesis in the cooling of flue gas) are not yet sufficiently advanced [3]. Therefore secondary measures are needed to lower the emissions of PCDD/PCDF once they are formed to such an extent that the limit value imposed is not exceeded. Here two fundamentally different technologies are applied in waste combustion facilities.

- Adsorption on a filtration material (fixed coke bed or carbon spray in the flue gas) [4].
- Catalytic oxidation with direct destruction of the PCDD/PCDF in the flue gas path [5,6]

Both systems have been proven for MWIs in European countries to enable stack gas values below 0,1ng I-TEQ/Nm³. For the former, the contaminated filtration material¹ needs an additional treatment to destroy the PCDD/PCDF, e.g. combustion of the coke or low temperature treatment under oxygen sufficiency [3]. For the latter, the SCR catalyst is a real sink for the PCDD/PCDF due to destruction of the compounds resulting in CO₂, H₂O and HCl [7].

In Europe and Japan, SCR catalysts are commercial available from different companies. Therefore for the producers of waste combustion facilities the question arises of which product to choose. Criteria of interest are (beside the price) the destruction efficiency and the temperature dependence of the destruction efficiency. One purpose of this study was to evaluate in what way a comparative laboratory study would provide insight in these questions and also evaluate the limitations of a laboratory testing.

Moreover, in laboratory studies scientific questions such as the dependence of destruction efficiency on chlorination degree or substitution pattern could be investigated in more detail. Additionally other classes of hazardous compounds with no regulation limits which therefore are normally not measured in field tests (e.g. PAH) could be taken into account.

Materials

Chemicals (all purchased from GL Science Inc., Japan - except PCDD/PCDF):

*Px*CBz: 1,2-D₂CBz, 1,2,3-T₃CBz, 1,2,4-T₃CBz, 1,2,3,4-T₄CBz, 1,2,4,5-T₄CBz, and H₆CBz.

¹ an advantage of the fixed coke bed is the additional adsorption of heavy metals

"Polyaromatic" compounds: Pyrene, Biphenyl, Dibenzofuran, and Dibenzodioxin
PCDD/PCDF: 1,3,6,8/1,3,7,9-T₄CDD (Synthesized via condensation of 2,4,6-T₃CP [8])
 2,4,8-T₃CDF (donated by Professor Hagenmaier, University Tübingen, Germany)
Catalysts: Three catalysts (V₂O₅, WO₃ on TiO₂ basis) of different Japanese producers (A,B,C).

Methods

The honey comb catalysts are crushed in pieces of about 2-5 mm to avoid leak streaming in the small quartz tube (13 mm internal diameter). The respective catalyst is put in the quartz tube of the flow reactor (Figure 1). The reactor is enclosed in a temperature-controlled furnace which provides a reactor temperature stability of $\pm 2^\circ\text{C}$. All ancillary tubing is maintained at a temperature of 150-200°C (in relation to catalyst temp.) with heating tape. The testing substances (about 1ug each) are applied to silica gel and put in the preheating system. After the reactor reaches stability at the respective temperature, the substances are evaporated resulting in an average concentration of about 1 ppm of aromatic compound. Temperature program: start at 70°C, hold for 5 min, 10°C/min to 160°C, hold for 15 min resulting in a total time of 30 min for the experiments. The gas mixture (10%O₂, 70%N₂, 20% H₂O) is regulated using mass flow controllers (Shinagawa Seiki, Japan). The reactor flow rate of 700ml/min corresponds to a space velocity (SV) of 5000 hr⁻¹ and is therefore comparable to those for SCR catalyst in MWIs. This results in a gas phase residence time in the catalyst bed of about 0.75 s.

After the experiment the glass tubes are rinsed with toluene these rinses are combined with the toluene in the washing bottle. The catalyst is extracted separately by 12h soxleth extraction with toluene.

Quantification was carried out on a HP 6890 gas chromatograph coupled to a HP 5973 mass selective detector with external standard calibration. The GC column used was a CP-SIL 88 column (50 m, 0.25 mm intern diameter, 0.2 μm film thickness, CHROMPACK, Frankfurt/FRG).

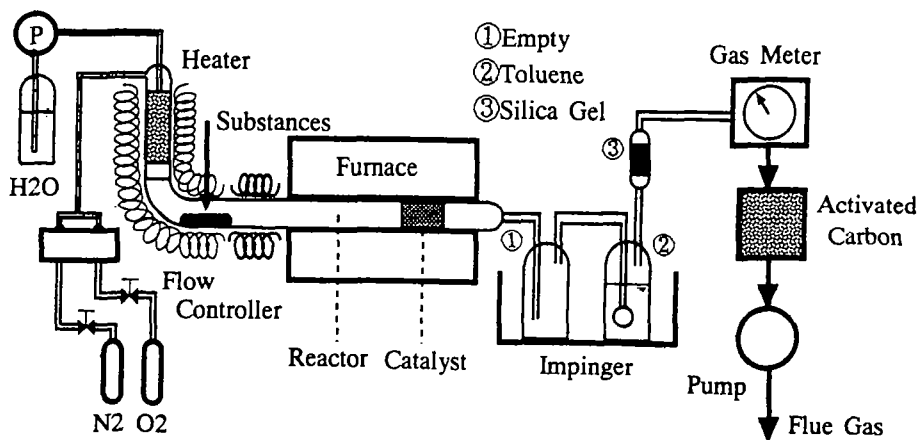


Figure 1: Experimental apparatus

Results

The destruction potency of the catalysts for PCDD/PCDF, polyaromatic hydrocarbons and polychlorinated benzenes (PxCBz) were compared in the temperature range of 150-310°C.

Chlorobenzenes:

Above 300°C the catalysts decompose more than 99% of the tested PxCBz (Figure 2). While at temperature below 200°C all three catalysts oxidize these compounds to an extent less than 50% (Figure 2).

The degree of chlorination does not have a decisive influence on the degree of destruction. With increasing chlorine substitution the catalytic decomposition increases and this is more emphasized at temperature below 200°C. This is surprising at first because the sensitivity for oxidation decreases with increasing chlorination degree (e.g. redox potential, ignition temperature, or oxidation in sulfuric acid). But with increasing degree of chlorination the volatility of a compound is considerably lowered resulting in longer residence time of the molecules in the catalytic chamber. This is confirmed by the fact that after the experiment at 150°C 4-10% of H₆CBz are detected on the catalyst after experiment while D₂CBz-T₄CBz were not detected (Figure 4). With chlorobenzenes therefore the effect of lowering the volatility with increasing chlorine substitution over-compensates the effect of the higher redox potential.

Regarding the destruction efficiency of the three catalysts, catalyst A exhibits lower decomposition rate than B and C which destroy PxCBz to almost the same extent (Figure 2).

When comparing the decomposition degree of the isomere of T₃CBz and T₄CBz (i.e. different substitution pattern with same degree of chlorination). The thermodynamic more stable 1,3,5-T₃CBz and 1,2,4,5-T₄CBz exhibit a lower destruction rate compared to the respective 1,2,3-T₃CBz and 1,2,3,4-T₄CBz. Additionally the latter exhibit the lower volatility ($\Delta b.p. \approx 10^\circ\text{C}$) which in our opinion exerts the bigger impact here.

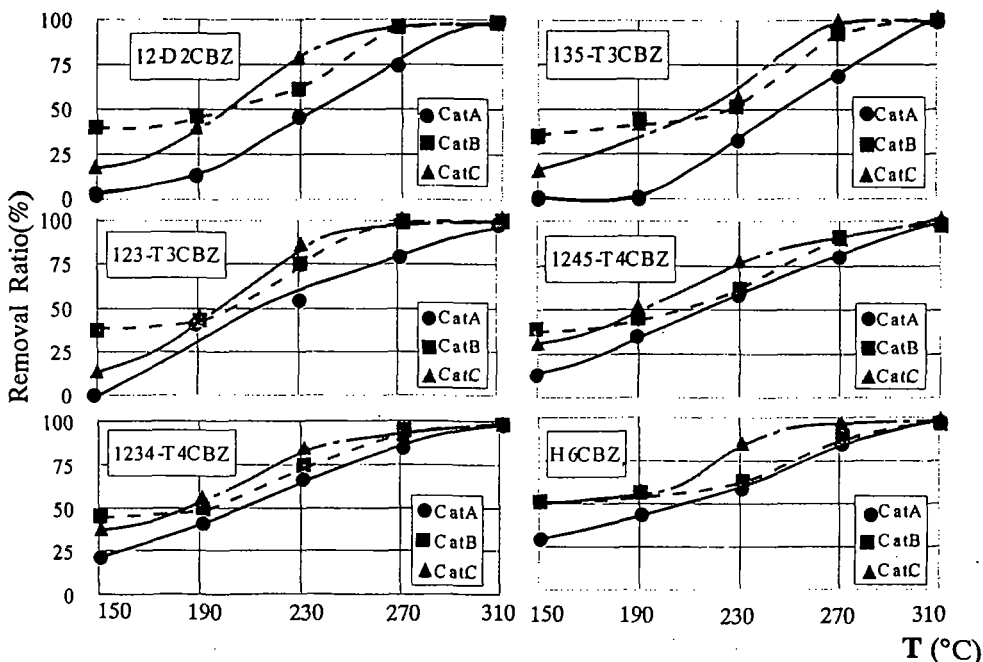


Figure 2: Removal rate of PxCBz after SCR catalysts (T: 150-310°C, 10% O₂, 20% H₂O, SV=5000 hr⁻¹)

"Polyaromatic" compounds:

When examining the concentration of the "polyaromatic" compounds found after catalyst, it appears that catalyst B and C decompose these molecules in the examined temperature range between 150 to 310°C with an efficiency of more than 95% - the most interesting compounds, the PCDD/PCDF even to an extent of more than 98% (Figure 3).

However in the experiments at 150°C 30-75% of the PCDD/PCDF remained on the catalysts (Figure 4), while at 190°C less than 7% of the PCDD/PCDF are found on the catalyst after the experiments. Therefore at temperature below about 190°C polychlorinated aromatic compounds endure on the catalyst for several minutes without being oxidized. At the chosen low concentration of 1ppm this phenomenon can not be explained by a leak of catalytic active centres. Therefore at this temperatures, the oxidizing potential of V_2O_5 and WO_3 is not sufficient to destroy polychlorinated aromatic compounds effectively. However the non chlorinated "polyaromatic" compounds are destroyed also at 150°C on catalyst B and C with an efficiency of more than 90% (Figure 3+4).

Contrary to the more volatile polychlorinated benzenes, the catalytic decomposition of the "polyaromatic" molecules decrease with increasing chlorine substitution at temperatures below 200°C. Here, the increase of the redox potential due to chlorination has a higher impact on the catalytic decomposition than the decreasing volatility. Therefore the penta- to octachlorinated dibenzodioxins and dibenzofurans, not considered in this investigation, probably will exhibit even lower decomposition rates than the Cl_3 - and Cl_4 -substituted congeners.

However for PCDD/PCDF at temperatures above 210°C these competing effects seem to balance each other as can be deduced from the unchanged homologue pattern during catalytic destruction of PCDD/PCDF in flue gas of MWI incinerators [4,5].

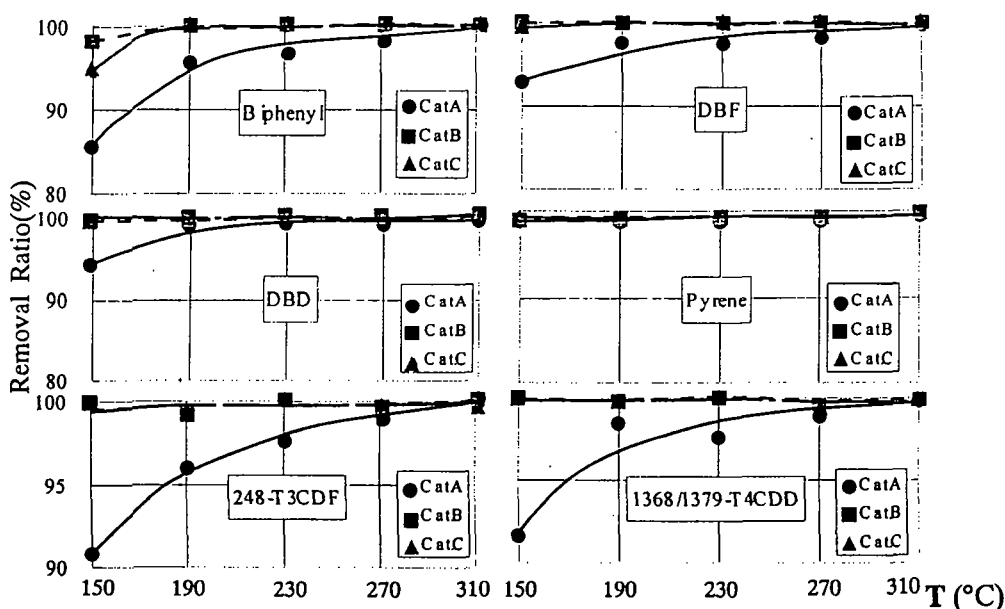


Figure 3: Removal rate of "polyaromatic" compounds after SCR catalysts (T: 150-310°C, 10% O_2 , 25% H_2O , $SV=5000 \text{ hr}^{-1}$)

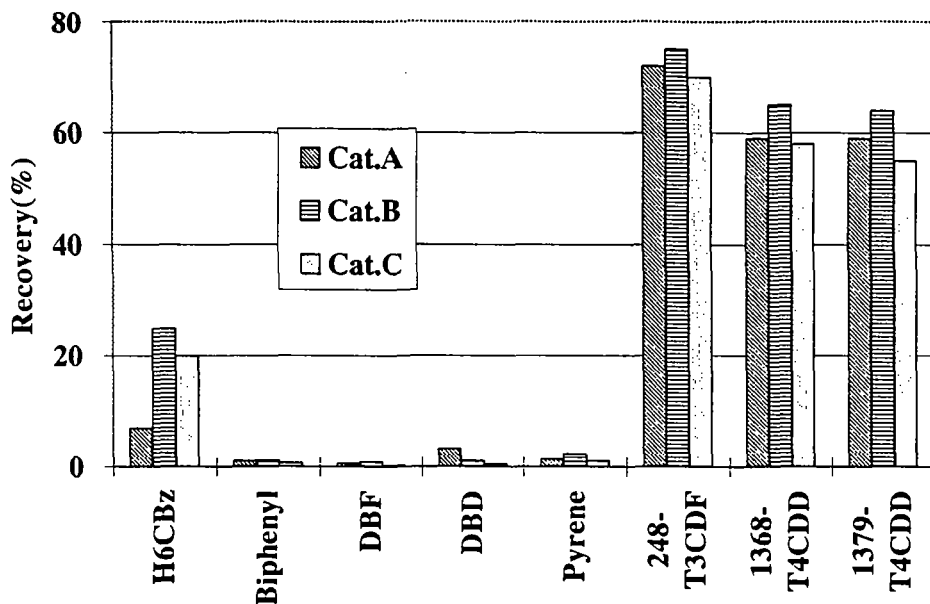


Figure 4: Recovery of adsorbed compounds on the catalysts after the experiments at 150°C

Discussion

According to these experiments catalyst B and C exhibits effective destruction for PCDD/PCDF above ca. 200°C. At operation temperature lower than 190°C the chlorinated "polyaromatic" compounds accumulate on the catalyst and after saturation would result in the release/no further adsorption of these compounds resulting in a low destruction degree.

For the effective destruction of monoaromatic compounds (chlorobenzenes, nitrobenzenes etc.) and volatile aliphatic and chlorinated aliphatic compounds, operation temperature higher than 250°C would be necessary.

Comparing these laboratory results with the recent endeavors for MWIs show a coincidence with the operation temperature aimed for PCDD/PCDF destruction.

Therefore the presented testing facility seem to be appropriate for testing and evaluating catalysts regarding the temperature dependence of destruction efficiency.

After changing these batch system into a flow reactor by supporting a constant stream of chlorinated hydrocarbons [7], these laboratory system should also enable the testing of thermal endurance of a catalyst or their sensitivity with respect to the Cl/O ratio which is relevant for the life time of a catalyst exposed to high concentration of chloride.

However with laboratory testing it is not possible to simulate the effect of the flue gas on the catalyst. Of special interest here is the examination of long term effect on the catalytic activity or the influence of the PCDD/PCDF destruction in relation to their distribution on particle phase and gas phase. In our opinion these topics can be investigated with meaningful evidence only in field tests.

References

- [1] The Advisory Committee for Controlling PCDDs/DFs in MSW Management. Guidline for Controlling PCDDs/DFs in MSW Management, **1997**.
- [2] M. Hiraoka, S. Sakai, T. Sakagawa and Y. Hata, *Organohalogen Compounds*, **1997**, 31,446.
- [3] H. Hagenmaier, K. Horch, H. Fahlenkamp, and G. Schetter, *Chemosphere* , **1991**, 23, 1429.
- [4] M. Eiken, J. Lambertz, and G. Ritter, *Umwelt - Zeitschrift des VDI*, **1990**, Heft 5, 226.
- [5] H. Hagenmaier and G. Mittelbach, *VGB Kraftwerkstechnik*, **1990**, 70, Heft 6.
- [6] H. Fahlenkamp, G. Mittelbach, H. Hagenmaier, H. Brunner, and K.-H. Tichaczek, *VGB Kraftwerkstechnik*, **1991**, 71, Heft 7.
- [7] H. Hagenmaier, *VDI Berichte*, **1989**, NR. 730, 239.
- [8] O. Aniline, *Adv. Chem. Ser.*, **1973**, 120, 126.