Role of DeNOx Catalyst in PCDD/F Emission Reduction in Hazardous Waste Incineration (HWI) Plant

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On the basis of nine periodical measurements, emissions of PCDD/F have been analysed. As a result, a correlation was detected between elevated PCDD/F emissions and operational problems with selective catalytic reduction (SCR) system.

The air pollution control system (APCS) consisted of dry scrubbing system (mixture of active carbon and NaHCO₃), fabric filter, DeNOx catalyst and wet scrubber. It was assumed that such a state-of-the-art system should be able to achieve dioxin emission limit of 0.1 ng Nm⁻³ I-TEQ, even without DeNOx catalyst. However, this expectation proved to be wrong.

The presence of memory effect was recognized as the possible cause of elevated PCDD/F emissions. During normal operational periods presence of memory effect was not noticed, due to selective catalytic reduction system. With malfunction of DeNOx catalyst, this effect escalated, causing elevated PCDD/F emissions.

Key words:
SCR, DeNOx, PCDD/F, memory effect

Introduction

In today’s turbulent environment shaped by globalization and the expansion of capital markets, quantities of waste are increasing rapidly, causing distortion of sustainability. Furthermore, irregular waste disposal becomes a serious threat to the environment and human health. Therefore, such huge amounts of waste need to be disposed safely. Today there are many waste treatment methods. One commonly known is thermal waste treatment. The primary benefit of thermal treatment is the substantial reduction of the mass (up to 75 %) and volume (up to 90 %) of waste. The generation of revenues from energy production, known as waste-to-energy treatment, can also partially offset the cost of treatment.

The waste incineration process results with formation of flue gases. Among CO₂ as a product of complete combustion of organic matter, flue gases can contain some other products of oxidation like solid particles, CO, HCl, HF, SO₂, NOₓ, heavy metals (Hg, Pb, Se, As, Sb, Cd, Ti, Ni, V etc.), volatile organic matter and chlorinated hydrocarbons (especially dibenzo-p-dioxins and dibenzofurans-PCDD/F). PCDD/F formation from incineration is known since 1977, when dibenzo-dioxins and dibenzo-furans were found in fly ashes and flue gases.¹ Thereafter efforts have been made to minimize the formation and emissions of dioxins from incineration facilities by means of primary measures, i.e. combustion control and secondary measures such as supply of different additives or use of special catalysts in the air pollution control system (APCS). One such technique for catalytic flue gas cleaning is selective catalytic reduction (SCR). SCR is the catalytic process which enables decomposition of NOₓ in flue gases to N₂ and water vapor in reaction with urea as a reduction agent. Commercial SCR catalyst is mostly composed of the oxides of Ti, V and W and is often used at a temperature range 300–400 °C.

The investigations show that the role of SCR in flue gas treatment from waste incineration plants is not limited only to NOₓ reduction.

In the late 1980’s it was incidentally found that SCR also decomposes polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F).² Additionally, in the last decade it was discovered that PCDD/F was oxidized by TiO₂/V₂O₅/WO₃ catalysts according to the following reactions:³

\[
\begin{align*}
C_{12}H_nCl_{8-n}O_2 + (9 + 0.5 \times n) O_2 & \rightarrow \text{TiO}_2/V_2O_5/WO_3 \\
& \rightarrow (n-4) H_2O + 12 CO_2 + (8-n) Cl (1)
\end{align*}
\]

\[
\begin{align*}
C_{12}H_nCl_{8-n}O_2 + (9.5 + 0.5 \times n) O_2 & \rightarrow \text{TiO}_2/V_2O_5/WO_3 \\
& \rightarrow (n-4) H_2O + 12 CO_2 + (8-n) HCl (2)
\end{align*}
\]

In addition, SO₂ and CO were also oxidized as shown in eqs. (3) and (4):

\[
\begin{align*}
SO_2 + 0.5 O_2 & \rightarrow \text{TiO}_2/V_2O_5/WO_3 \\
& \rightarrow SO_3 (3)
\end{align*}
\]

\[
\begin{align*}
CO + 0.5 O_2 & \rightarrow \text{TiO}_2/V_2O_5/WO_3 \\
& \rightarrow CO_2 (4)
\end{align*}
\]
However, on the catalyst surface the following reactions may also occur:

\[
\begin{align*}
\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} & \rightarrow \text{NH}_4\text{HSO}_4 \\
2\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} & \rightarrow (\text{NH}_4)\text{}_2\text{SO}_4
\end{align*}
\] (5) (6)

Ammonia salts deposited on the catalyst surface can cause a decrease in the catalyst’s activity. That process is temperature dependent and reversible. Thus, heating up the flue gas stream before entering the catalyst module to temperatures higher than 290 °C, may enable catalyst reactivation.

The main purpose of this research was to investigate the PCDD/F emission problems occurring at the hazardous waste incineration plant PUTO in Zagreb, Croatia. The research results are presented in this article.

**Materials and methods**

**The incineration plant**

Incineration plant PUTO, Zagreb, Croatia, was used for incineration of hazardous and non-hazardous industrial waste assays. The plant is designed for incineration of 1200 kg h⁻¹ of waste, of net calorific value 20930 kJ kg⁻¹ (~5000 kcal kg⁻¹).

The incineration system consists of two modular process units: rotary kiln (RK) and post combustion chamber (PCC).

Before entering APCS, the flue gas stream is cooled down by mixing it with cold air. Flue gases leaving the post combustion chamber (PCC) with a temperature between 1000 and 1200 °C, are mixed with cold air and cooled down to 850 °C before entering the system of air cooled heat exchangers.

Heat exchangers (HE) 1 and 2 operate in parallel and the flue gases split into two streams (because of their large volume) and are cooled down to about 350 °C. After HE 1 and 2, the flue gas stream passes through HE 3, where the flue gas is cooled further to about 220 °C.

The APCS is designed as a dry or wet operation system, depending on chlorine and sulphur mass concentration in the waste feed. Process flow diagrams are shown in Figs. 1 and 2.

Dry system should be used for lower content of Cl and S. It was estimated that the plant should work for about 90–95 % of the time in a dry regime.

In the dry operation system, flue gases are cooled down to 220 °C and are directed to the reactor (RC). In the RC, a mixture of sodium hydrogen carbonate (NaHCO₃) and activated carbon is added to the flue gas stream.

In the case of the wet regime, water from the scrubber system is sprayed down in the reactor. The water evaporates, while salts and other polluting substances are removed from the system in the bag filter (BF). In this regime, the temperature of the flue gases at entrance into the reactor is about 350 °C, and the HE 3 is shut down.

![Process flow diagram – dry system](image)
NaHCO₃ and activated carbon are added directly into the flue gases pipeline just after the reactor exit.

The bag filter consists of three modules with 480 Teflon bags resistant to temperatures up to 250 °C. This allows the removal of the solid particles with efficiency up to 99.9 %, and other gaseous pollutants with efficiency up to 99.5 %.

Removal of the deposits from the bag filters is performed by a “pulse-jet” system using compressed air. Deposits, consisting of fly ashes and a mixture of NaHCO₃ and activated carbon are collected in large bags, and stored for final disposal.

The role of the bag filters in APCS is not just the removal of solids from flue gases. On the surface of the bag filter, a filter cake is formed. This cake consists of solid reagents (NaHCO₃ and activated carbon) and provides excellent contact between the flue gas stream and activated carbon, provoking high removal (up to 99.5 %) of HCl, HF, SO₂, volatile heavy metals (such as Hg, Cd, Tl, Se, As), polychlorinated biphenyls (PCB), polycyclic aromatic hydrocarbons (PAHs) and PCDD/F.

When exiting the bag filters, the flue gases pass through HE 4 for reheating this stream to a temperature of about 320 °C, by using hot air from HE 1 and 2. Further on, the flue gases go to the SCR DeNOx stage, which uses urea as a reducing agent.

The SCR DeNOx unit is a commercial monolith catalyst produced by Porzellanfabrik Frauenthal GmbH, Austria consisting of TiO₂ and some impurities (see Table 1). Although mass concentrations of PCDD/F in the flue gas stream at the exit of the bag filter are very low, in the presence of the catalyst these mass concentrations are even lower.

After the SCR DeNOx unit, and in the dry regime, the flue gases are conveyed to the stack. In the wet regime, flue gases are conveyed to the wet scrubber system. The first scrubber column is used for acid washing, and HCl and HF removal. The second is designed for alkaline washing, removal of Cl, HF and SO₂. From the scrubber system, the flue gases are conveyed to the stack.

<table>
<thead>
<tr>
<th>Table 1 – Physical and chemical properties of catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical characteristics</strong></td>
</tr>
<tr>
<td>number of modules, N</td>
</tr>
<tr>
<td>dimensions of module, l/mm</td>
</tr>
<tr>
<td>specific volume of pore, s/m² g⁻¹</td>
</tr>
<tr>
<td>volume of pore, v/cm³ g⁻¹</td>
</tr>
<tr>
<td><strong>Chemical composition</strong></td>
</tr>
<tr>
<td>V₂O₅, w%</td>
</tr>
<tr>
<td>SO₃, w%</td>
</tr>
<tr>
<td>K₂O, w%</td>
</tr>
<tr>
<td>Na₂O, w%</td>
</tr>
<tr>
<td>TiO₂, w%</td>
</tr>
</tbody>
</table>
PCDD/F measurements

Flue gas emissions were measured continuously and periodically. The following substances were continuously measured: NO\textsubscript{x}, CO, CO\textsubscript{2}, total dust, TOC, HCl and SO\textsubscript{2}. In addition, HF, volatile heavy metals and PCDD/F, were measured twice a year. During all periodic measurements, hazardous waste of known characteristics was incinerated, and the incineration plant worked in a dry regime. PCDD/F sample preparation and analysis were made according to DIN EN 1948.

Results and discussion

Table 2 shows emission concentrations of the PCDD/F measured at the stack. The periodic measurement reports No. 4 (June, 1998), No. 5 (April, 22\textsuperscript{nd} 1999) and No. 6 (April, 23\textsuperscript{rd} 1999), do not contain mass concentrations of individual congeners, so they are excluded from the table.

Table 2 – Emission mass concentrations of the PCDD/F measured at the stack

<table>
<thead>
<tr>
<th>Congeners</th>
<th>Measurement number</th>
<th>Date of measurement</th>
<th>γ/pg Nm\textsuperscript{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>2,3,7,8 TCDD</td>
<td>0.253</td>
<td>0.271</td>
<td>0.279</td>
</tr>
<tr>
<td>1,2,3,7,8 PeCDD</td>
<td>0.506</td>
<td>0.542</td>
<td>1.955</td>
</tr>
<tr>
<td>1,2,3,4,7,8 HxCDD</td>
<td>0.506</td>
<td>0.542</td>
<td>3.352</td>
</tr>
<tr>
<td>1,2,3,7,8,9 HxCDD</td>
<td>1.013</td>
<td>1.084</td>
<td>3.073</td>
</tr>
<tr>
<td>1,2,3,6,7,8 HxCDD</td>
<td>1.772</td>
<td>1.897</td>
<td>6.425</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8 HxCDD</td>
<td>13.671</td>
<td>14.634</td>
<td>48.045</td>
</tr>
<tr>
<td>OCDD</td>
<td>42.785</td>
<td>45.799</td>
<td>149.162</td>
</tr>
<tr>
<td>2,3,7,8 TCDF</td>
<td>1.013</td>
<td>1.084</td>
<td>5.307</td>
</tr>
<tr>
<td>2,3,4,7,8 PeCDF</td>
<td>3.291</td>
<td>3.523</td>
<td>12.011</td>
</tr>
<tr>
<td>1,2,3,7,8 PeCDF</td>
<td>1.266</td>
<td>1.355</td>
<td>5.587</td>
</tr>
<tr>
<td>1,2,3,4,7,8 HxCDF</td>
<td>4.557</td>
<td>4.878</td>
<td>17.039</td>
</tr>
<tr>
<td>1,2,3,7,8,9 HxCDF</td>
<td>0.506</td>
<td>0.542</td>
<td>1.955</td>
</tr>
<tr>
<td>1,2,3,6,7,8 HxCDF</td>
<td>4.051</td>
<td>4.336</td>
<td>16.48</td>
</tr>
<tr>
<td>2,3,4,6,7,8 HxCDF</td>
<td>6.835</td>
<td>7.317</td>
<td>26.816</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8 HxCDF</td>
<td>63.291</td>
<td>67.751</td>
<td>240.223</td>
</tr>
<tr>
<td>1,2,3,4,7,8,9 HxCDF</td>
<td>3.544</td>
<td>3.794</td>
<td>10.056</td>
</tr>
<tr>
<td>OCDF</td>
<td>54.43</td>
<td>58.266</td>
<td>217.877</td>
</tr>
</tbody>
</table>

γ(PCDD/F) ng Nm\textsuperscript{-3} I-TEQ 0.019 0.023 0.068 0.00664 0.1088 0.0622 7.4 7.2 1.3629

Elevated mass concentrations of PCDD/F in flue gas correlated with operational problems of the SCR DeNOx system. Problems with the SCR DeNOx system started only six to eight months after the plant became fully operational, and they can be described as:

– Corrosion products from the upper and side walls of the catalyst module blocked the inlet of the unit;

– Erosion of the catalyst layer underneath the nozzle for urea spraying, caused by trickling of urea from the nozzle onto the catalyst, or due to bad dispersion of urea in the flue gas stream.

In the beginning of 2001, the pressure drop across the catalyst increased to the point where ventilator at HE 4 could not provide vacuum in the system, and all the attempts to clean it did not have positive results. According to the recommendations of the licensee and other available information, it was assumed that the plant with such a state-of-the-art APCS could easily, even without the SCR...
DeNOx system, achieve PCDD/F emissions below the EU emission limit of 0.1 ng Nm\(^{-3}\) I-TEQ. Hence, it was decided to put the SCR system out of operation. The expectation proved to be wrong.

On the first periodical measurement conducted just after turning of the SCR DeNOx unit (May 2001), elevated mass concentrations of PCDD/F were measured, reaching an average value of 7.4 ng Nm\(^{-3}\) I-TEQ. After analyzing these preliminary measurements, it was obvious that the DeNOx catalyst had a significant influence on PCDD/F reduction in the PUTO incineration plant. The next measurement campaign was carried out in October 2001, and similar mass concentrations of PCDD/F were determined: 7.2 ng Nm\(^{-3}\) I-TEQ. Thereupon, several measures were implemented for the reduction of PCDD/F emissions:

- Stringent control of the entire incineration process (temperatures in the RK and PCC, continuous emission measurement- 1/2 hour and daily values);
- Only waste with up to \(w = 1\%\) of Cl was accepted for incineration;
- Reparation of upper walls and cleaning of HE 1 and HE 2.

All these measures resulted in a slight decrease of PCDD/F mass concentration. PCDD/F measurement carried out in June 2002 indicated an average value of 1.36 ng Nm\(^{-3}\) I-TEQ, still exceeding the emissions limit.

Fig. 3 shows the mass concentrations of the so-called “dirty 17” PCDD/F congeners, during operation with DeNOx catalyst.

Fig. 4 shows fractions of PCDD/F homologues, during operation with DeNOx catalyst.

Profiles of PCDD/F congeners and homologues shown in Figs. 3 and 4 refer to the typical “fingerprint” from combustion processes:

- PCDD : PCDF ratio is larger than 1 (0.566 : 0.434);
- Fractions of the homologues increases with the degree of chlorination for PCDDs, and shows a maximum at PeCDF, HxCDF or HpCDF;
- The isomer pattern contains every isomer, with major presence of OCDD, 1,2,3,4,6,7,8-HpCDF and OCDF.

After the DeNOx catalyst was put out of function, three periodical measurements were made. Their results are shown in Fig. 5.

Comparison of the results with and without the catalyst, shows changes in percentage of the 2,3,7,8-substituted PCDD/F congeners. Major presence of HpCDD, OCDD, HpCDF and OCDF can still be observed. Fractions of HxCDF and the ratio of HpCDF and OCDF increased greatly in comparison with measurements made when the catalyst was functional.
In addition, mass concentrations of some congeners increased by about one or two orders of magnitude.

Comparison of the results in Figs. 3 and 5 shows major presence of PCDF congeners in measurements without the catalyst (Fig. 3). The PCDD : PCDF ratio is now 0.753 : 0.247.

Table 3 shows the average mass concentrations of PCDD/F congeners measured with and without the catalyst, and congener ratio of percentages.

According to the results in Table 3, it is obvious that there was a significant increase in percentage of lower chlorinated 2,3,7,8-substituted congeners PCDD/F. In case of dioxins, the ratio of 2,3,7,8-TCDD increased 88 %, and 1,2,3,7,8-PeCDD 54 %, while the other PCDD congeners had a smaller ratio.

In the case of furans, an increase in the ratio OCDF and 1,2,3,7,8,9 HxCDF may be observed, while the largest increase was observed for lower chlorinated congeners.

This change can be seen even better in the comparison of the homologues from tetra to octa PCDD/F for measurements with and without DeNOx catalyst. The results of this comparison are shown in Table 4.

It is clear that there is a change in the ratio for TCDD of 4.2 times, and PeCDD of 1.07 times.

In the case of furans, TCDF increased 3.69 times, and PeCDF 2.32 times.
Figs. 6 and 7 show the average fraction of PCDD/F homologues for the measurements with and without DeNOx catalyst.

Fraction distribution of PCDD/F homologues shown in Figs. 6 and 7, clearly shows possible presence of the so-called memory effect. Memory effect is caused by adsorption of PCDD/F on some favorable parts of APCS, usually on the plastic scrubber fillings, when the formation and emission of PCDD/F from incinerator is high. The adsorbed dioxins are then slowly desorbed when the plant is running under more stable conditions. The presence of the memory effect can be noticed from the variation of homologue and congener profiles across the critical section.

Adsorption and desorption phenomena of PCDD/F are governed by the vapor pressure. In the presence of the memory effect, lower chlorinated PCDD/F congeners are more easily desorbed and are expected to increase in the flue gas exiting the critical part of the plant.

Recent researches show that the same phenomena can be noticed on the cold side of the recovery section, or even deposits of residual carbon on the duct walls, which contain dioxin, dioxin precursors and catalyst such as Cu and Fe, can eventually increase the dioxin concentrations in the flue gas. Significant persistence of the dioxin emissions was found, indicating both the extent of the residual, or memory effect and the persistent reactivity of the deposits. These soot deposits may act as a source of PCDD/F emissions, particularly after a period of poor combustion conditions.

In favor of the presence of the memory effect is the fact that the plants with APCS consisting of dry scrubber (injection of active carbon and Ca(OH)2 or NaHCO3) in combination with bag filter, have a dioxin removal efficiency typically about 97.0 to 99.9% meaning they can easily achieve emission limits well below 0.1 ng Nm−3 I−TEQ. If the memory effect was not present, the PUTO incineration plant, even without DeNOx catalyst, would be able to work in the range far below the emission limits.

Increase in mass concentrations of some PCDF congeners can partly be explained by putting the DeNOx catalyst out of function, because SCR systems induce the reduction in portion of PCDF. It is because the SCR system shows higher efficiency in the removal of furans than dioxins from the flue gas.

According to the results in Table 3, the percentage of furans measured with DeNOx catalyst was 0.649, in comparison with 0.752 measured without the catalyst.

Other possibilities that could influence increased PCDD/F were considered, such as bag filter damage or malfunction in the system of activated carbon injection.

Leakage in the bag filter could lead to increased PCDD/F emissions in flue gas. However, in this case other emission parameters would also be increased (dust, heavy metals etc.). In addition, the pressure drop across the bag filter section would be decreased, but that was not observed.

If the activated carbon injection system should malfunction, the emission of heavy metals, Hg or TOC would also increase throughout a longer working period, but that also was not observed.

**Conclusions**

The high PCDD/F mass concentrations in flue gas corresponds to operational problems of DeNOx system, implying that DeNOx catalyst has a significant influence not only on the reduction of NOx, but also on the removal of PCDD/F from the flue gas.

The probable cause of the high PCDD/F emissions found after the removal of the DeNOx system was the presence of fly ash in certain parts of flue gas ducts, due to poor maintenance of the facility, resulting in occurrence of the memory effect. During normal operation periods this was not observed, due to the selective catalytic reduction system. When the DeNOx system was shut down, the presence of the memory effect resulted in elevated PCDD/F emissions.
List of symbols

- $l$ – dimension of modul, mm
- $N$ – number of moduls
- $s$ – specific surface of catalyst, m$^2$ g$^{-1}$
- $v$ – specific volume of pore, cm$^3$ g$^{-1}$
- $w$ – mass fraction
- $\gamma$ – mass concentration, ng Nm$^{-3}$
- $\xi$ – mass ratio

List of abbreviations

- APCS – air pollution control system
- BF – bag filter
- HE – heat exchanger
- I-TEQ – International Toxic Equivalent
- PAHs – polycyclic aromatic hydrocarbons
- PCB – polychlorinated biphenyls
- PCC – post combustion chamber
- RC – reactor
- RK – rotary kiln
- SCR – selective catalytic reduction
- TOC – total organic carbon
- TCDD – tetrachloro-dibenzo-dioxins
- PCDD/F – polychlorinated dibenzo-p-dioxins and dibenzofurans
- PeCDD – pentachloro-dibenzo-dioxins
- HxCDD – hexachloro-dibenzo-dioxins
- HpCDD – heptachloro-dibenzo-dioxins
- OCDD – octachloro-dibenzo-dioxins
- TCDF – tetrachloro-dibenzo-furans
- PeCDF – pentachloro-dibenzo-furans
- HxCDF – hexachloro-dibenzo-furans
- HpCDF – heptachloro-dibenzo-furans
- OCDF – octachloro-dibenzo-furans

References