CATALYTIC FILTER APPLICATION IN THE TERMIZO MUNICIPAL WASTE INCINERATION PLANT IN LIBEREC

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History of the Incineration Plant

The municipal waste incineration plant Termizo a.s. in Liberec (Czech Republic) started operation in the year 1999. Its capacity is 96 000 tons of the waste per year, with planned operation time of 8 000 hours per year. The thermal output of the plant is ca. 23 MW and the electric output of the back-pressure steam turbine is 2.5 MW. The combustion chamber consists of a stoker-fired furnace and an afterburning chamber with three vertical radiation ducts and one horizontal convection duct. The furnace temperature varies between 950 and 1100°C, the temperature in the afterburning chamber exceeds 850°C and the retention time of the combustion products is longer than 2s. Ammonia liquor, 25 wt. %, is added to the upper part of the first vertical duct, for selective non-catalytic reduction of nitric oxides (SNCR). The afterburning chamber is followed by an electrostatic precipitator, REMEDIA® D/F Catalytic Filter System and a three-stage flue gas scrubber, involving a water quench, absorption of sulfur oxides in sodium hydroxide and aerosol separation – a Venturi jet. The present technology for PCDD/F removal has been installed in the incinerator since September 2003. During the period of 2001 - 2003, the incinerator used addition of a solid sorbent based on powdered activated carbon (PAC) to the combustion products. The incinerator is schematically depicted in Fig. 1. The average emissions of the incinerator during the period from September 2004 to September 2005 are given in Table 1. and compared with the emission limits.

Figure 1. Flow sheet of TERMIZO MWI in Liberec

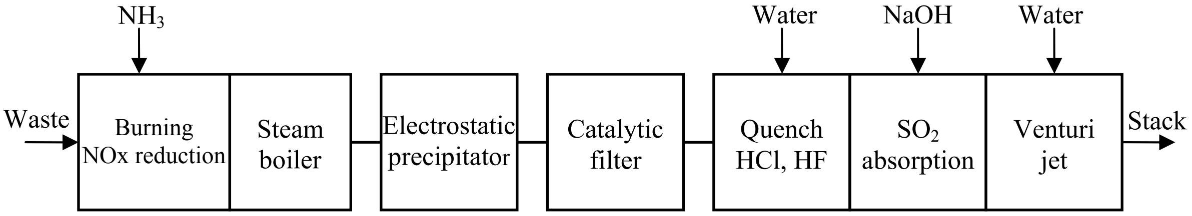

Table 1. Average stack emissions from September 2004 to September 2005

Flue gas volume m_N^3/h	O_2 Vol-%	CO mg/m_N^3	SO_2 mg/m_N^3	NOx mg/m_N^3	HCl mg/m_N^3	Dust mg/m_N^3
62400	9.81	4.52	13.5	194	0.24	0.30
Czech daily emission limits (mg/m_N^3)		50	50	350	10	10

Materials and Methods

The REMEDIA® D/F Catalytic Filter System is supplied by W.L.GORE & Associates GmbH. This a double-layer catalytic filter, operating on the principle of oxidative catalytic destruction of PCDD/F. The outer layer consists of a PTFE GORE-TEX® membrane and collects solid particles. The inner felt layer of expanded PTFE with a catalyst based on TiO_2-anatase/V_2O_5, WO_3 is patented under the name RASTEX® and serves for catalytic destruction of PCDD/F[1]. The Liberec incinerator employs 676 filter bags with the overall filter area of 1800 m^2. The operation temperature of the catalytic filter varies within 200 - 220°C.

The contents of polychlorinated benzenes (PCBz), polychlorinated phenols (PCPh) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) were determined according to the ČSN EN 1948 standard.

Results and Discussion

The placing of the catalytic filter behind the electrostatic precipitator in raw flue gas, with additional preceding selective non-catalytic reduction of NOx, is a unique application of this technology that involves certain risks that are primarily connected with the preceding SNCR unit. The use of the catalytic filter requires minimization of the excess of ammonia from the flue gases in SNCR. The excess ammonia may be converted into ammonium salts (e.g. hydrogensulfate and chloride) that might form hygroscopic layers mechanically blocking the catalytic filter. On this basis, dosing of a suitable zeolite before the catalytic filter will be tested in the incineration plant. The zeolite should be injected into the flue gases periodically, every twelve hours, after pulse cleaning of the filter. The surface active zeolite will form a protective microlayer on the surface of the catalytic filter, preventing adhesion of hygroscopic, adhesive ammonia compounds and their irreversible penetration into the micropores of the filter.

In contact with the active component of the catalytic filter, ammonia may also enhance undesirable reduction of nitric oxides. Addition of ammonia is regulated according to the determined actual stack concentration of NOx. The amount of the ammonia liquor varied within 20 to 80 l/h. Due to a change in the regulation algorithm in May 2005, these values decreased to 15 to 27 l/h. The ammonia concentration at the catalytic filter inlet varied within 0.6 - 6.5 mg NH_3/m_N^3, the outlet concentration was 0.4 - 4.5 mg NH_3/m_N^3. The determinations that were carried out indicated a slight decrease in the ammonia concentration on passage through the catalytic filter, caused probably by its reaction with nitric oxides. The NOx concentrations were determined in flue gases, without adding ammonia liquor, obtaining ca. 300 - 350 mg NOx/m_N^3 in raw flue gases. The balance has indicated that an increase in the amount of ammonia liquor added by ca. 10 l/h should cause an increase in the ammonia concentration on the catalytic filter by ca. 150 - 200 mg NH_3/m_N^3. However, this disagrees with the amounts of ammonia measured by us on the filter, because ammonia regulation based on NOx stack emissions is complex and probably lead to partial overdosing. This disagreement is caused by competing ammonia reactions in which nitrogen and possibly also undesirable nitrogen(II) oxide are formed[2]. This is a further reason for the importance of avoiding overdosing of ammonia in the incinerator.

On TiO_2/V_2O_5, WO_3 based catalysts, the formation of N_2O by the oxidation of ammonia[3] has been found. Our measurements lead us to the conclusion that this effect does not occur on the catalytic filter of the Liberec incinerator because the N_2O concentrations before and after the catalytic filter never exceeded the analyzer detection limit, 2 ppm, during incinerator operation under steady-state regime.

An analysis of a catalytic filter sample was carried out after ca. 15 000 hours of the filter operation. From the results it follows that dust particles did not penetrate into the filter and were absent in its inner layer. Dust was only present on the surface of the outer, non-catalytic layer. The catalytic activity did not decrease after 15 000 hours of the filter operation. The Energy Dispersive X-ray analysis of the dust from the filter surface indicated the presence of NH_4HSO_4, which is adhesive, hygroscopic substance formed by the reaction of the excess ammonia from SNCR with the SO_2 from the flue gases[4]. This is surprising, because at temperatures around 220°C, which is close to the upper limit of the operation range of this catalytic filter, deposition of NH_4HSO_4 should not occur[5]. The filter is now periodically pulse cleaned, every twelve hours, without effect on its pressure loss. This is due to the small amount of dust that does not affect the pressure loss. The pressure loss slightly increased during the first year of the filter operation and then remains virtually constant.

To determine the overall load of the catalytic filter, further chlorinated organic aromatic compounds that are assumed to be precursors of PCDD/F were monitored in the flue gases, namely, polychlorinated benzenes and polychlorinated phenols.

Under steady-state regime, the PCBz concentrations in the flue gases vary between 1.0 and 1.5 μg/m^3, immediately after shutdown of the operation, the PCBz concentration was up to 8.1 μg/m^3, which is a 5 to 8fold increase compared to the steady state. During the days following the interruption, the PCBz concentrations in the flue gases gradually decrease, down to the steady-state value prior to the shutdown. The removal efficiency of the filter was between 3 and 25 % for chlorobenzenes in most of the experiments, which is in agreement with the findings of Ide[6] et al. who found a decrease of 8.8 to 30 % in the chlorobenzenes content in municipal waste incineration plant flue gases, in a test apparatus employing a TiO_2-V_2O_5-WO_3 catalyst at a temperature of 210°C. Sakurai[7,8] et al. found a destruction efficiency for chlorobenzenes within the range of 50 to 70 % at temperatures of 200 to 220°C on commercial catalysts for NOx reduction based on TiO_2-V_2O_5-WO_3. PCBz is assumed to involve the sum of tri- to hexachlorinated benzenes, mono- and dichlorinated benzenes are not considered. The results of the PCBz analyses are given in Fig. 2.

The determination of PCPh, considered as important precursors of PCDD, in the flue gases yielded concentrations of 1.7 - 6.5 μg/m^3 prior to the catalytic filter and 0.13 - 0.17 μg/m^3 after it, which corresponds to the catalytic filter removal efficiency of 90 - 98 %. Similar results were obtained by Ide[6] et al. who also found efficiencies between 90 and 98 % in a test apparatus with a TiO_2-V_2O_5-WO_3 catalyst.

It is known from measurements on raw flue gases, that under steady-state regime of the incinerator, the PCDD/F concentrations vary within 1.0 - 1.5 ng TEQ/m_N^3. Higher values in raw flue gases were found during first two years of the incinerator operation, namely, 2.0 - 5.7 ng TEQ/m_N^3. Since August 2001, the incinerator employed PCDD/F removal technology based on injection of powdered activated carbon into the flue gases injecting amounts of ca. 5 kg/h and removing them in a wet flue gas scrubber. This technology enabled a decrease in the PCDD/F emissions to 0.18 - 0.37 ng TEQ/m_N^3, which is, however, 2 to 4times higher than the emission limit for these substances, decreed by the government of the Czech Republic at 0.1 ng TEQ/m_N^3. A further drawback of PAC injection into the flue gases is the fact that PCDD/F are not destroyed but only adsorbed on the activated carbon. The contaminated carbon then becomes a dangerous waste whose further liquidation is economically demanding. For these reasons, this technology was replaced in September 2003 by a new one, REMEDIA® D/F Catalytic Filter System, combining surface filtering with catalytic destruction. From this date, the PCDD/F stack emissions amount to 0.013 - 0.031 ng TEQ/m_N^3, i.e., are 3 to 8times lower than the Czech emission limit and ca. 10 to 30times lower than the concentrations obtained by PAC injection. It is evident that the REMEDIA® D/F Catalytic Filter System technology enables easy compliance with the PCDD/F emission limit according to the Czech regulations. A historical survey of the PCDD/F stack emissions from the incinerator is given in Fig. 3. Table 2. evaluates the behavior of the components monitored during the passage through the filter.

The described measured constitute the first stage of incinerator modernization and the problems discussed are further treated.

Figure 2. The behavior of PCBz on the filter and the effect of incinerator shutdown on their concentrations in the flue gases

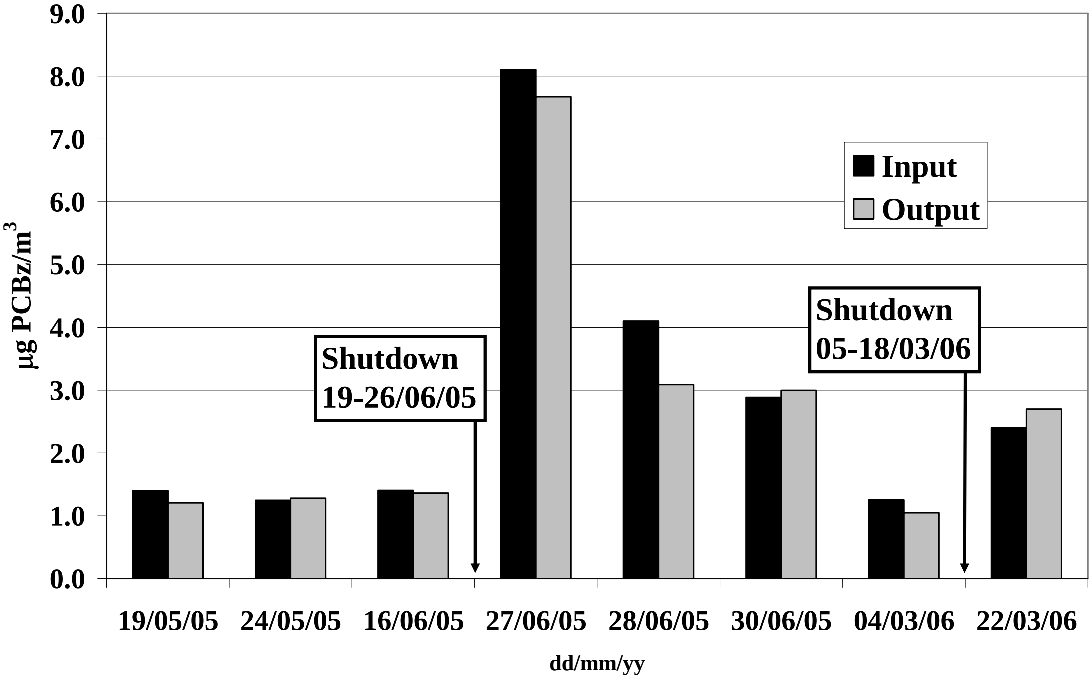

Figure 3. PCDD/F stack emissions

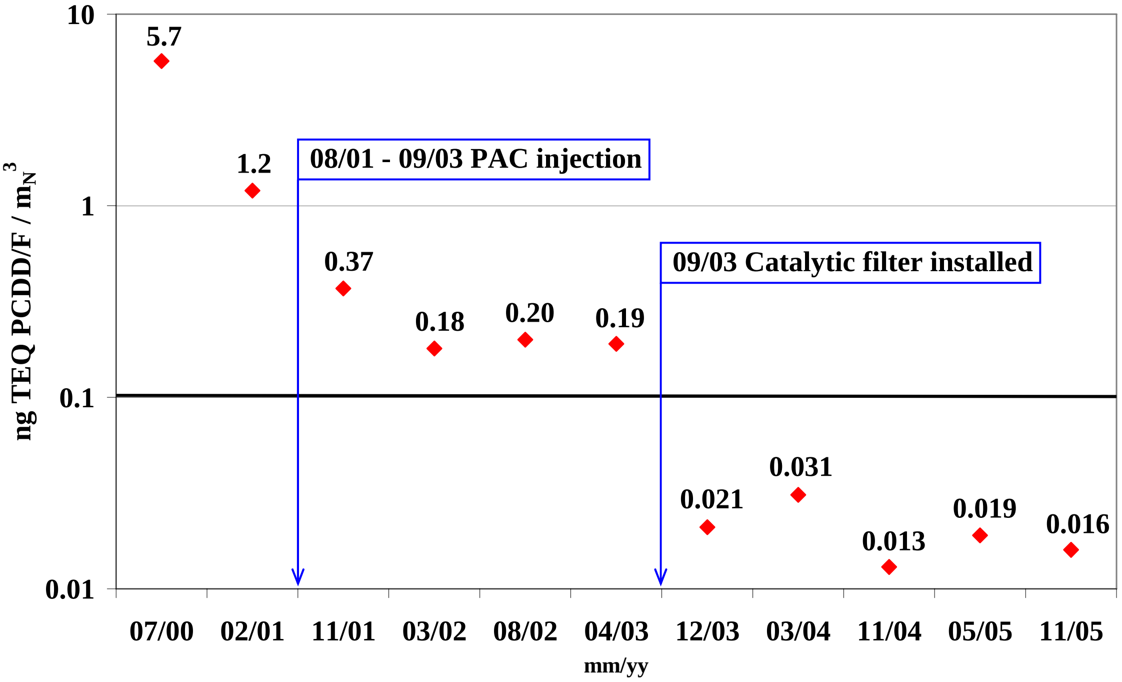

Table 2. Behavior of selected components on the filter during steady-state regime of the incinerator

	NH_3 (mg/m_N^3)	**N_2O** ppm	**PCBz** ($\mu g/m^3$)	**PCPh** ($\mu g/m^3$)	**PCDD/F** (ng TEQ/m_N^3)	**Dust** (mg/m_N^3)
Input	0.6 - 6.5	< 2	1.0 - 1.5	1.7 - 6.5	1.0 - 1.5	10 - 50
Output	0.4 - 4.5	< 2	1.0 - 1.5	0.13 - 0.17	0.013 - 0.031	1 - 2

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