CHEMICAL ENGINEERING TRANSACTIONS, Volume 12, 2007
Edited by Jiri Klemeš
 ISBN 88-901915-4-6

Reduction of Persistent Pollutants Emissions

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Generation of wide range of harmful compounds as a result of waste incineration represents a problem which has to be solved in agreement with environmental regulations. Flue gas contains the following groups of harmful compounds: persistent organic pollutants (POP), especially enormously toxic polychlorinated dibenzo-p-dioxins a polychlorinated dibenzo-furans (PCDD/F).
Based on experience from operation of the incinerator with capacity of 96,000 t/y it has been proved that even after more than three year's operation the activity of filtration material was not decreased and efficiency of dioxins removal from flue gas ranges from 97 to 99 %. These facts come from complex measurements where concentration of PCDD/F toxic congeners in both flue gas and separated flying ash was measured. We arrived at confirming expected assumptions that various congeners are not decomposed uniformly in the dioxin filter and the stage of their decomposition depends on their representation in the gas phase. It is strongly influenced by their molecular weight.

Keywords PCDD/F, dioxins, catalytic filtration, municipal solid waste,

1. Introduction

During incineration of municipal and industrial waste flue gas containing harmful components (off-gas) is created. These have to be efficiently removed before they enter the ambient [Council Directive 2000/76]. Sufficiently low levels of most of the unwanted components can be reached by common methods of absorption and adsorption gas cleaning. The most toxic components contained in flue gas created by combustion of municipal solid waste (MSW) and industrial waste are polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/F, also known as "dioxins"). Raw flue gas from municipal incineration plants contains a whole range of isomers of dioxin related components with various toxicity, where the equivalent toxicity (converted to 2,3,7,8 TCDD) usually reaches values between 1 to 5 ng TEQ/m_N. The strongly toxic character of this group requires very effective removal of these pollutants and remaining concentrations should be at the lowest possible level, which has been set by the European Union set to max. 0.1 ng TEQ/m_N^3 in 1994. Without and additional unit for the removal of dioxins it is almost impossible to satisfy these emission limits. For the reduction of POP emissions and comply with

the emission limits a number of widely used methods [Buekens, 1998] exists. For industrial applications are mainly used methods of cleaning gas with adsorbents or methods of catalytic decomposition.

Reduction of dioxins concentration in the flue gas in many cases is reached by adsorption techniques using active carbon injection (the dosage is about 50 to 100 mg/m_N^3) or passing the flue gas through a moving bed of fixed bed of active coal. The adsorbent can be mixed with others sorbents ($Ca(OH)_2$, $NaHCO_3$, etc.). The PCDD/F removal efficiencies of adsorption methods can be more than 90 % effective, but a disadvantage of adsorption methods, which have lower investment and operation costs than catalytic decomposition, is the fact that pollutants from gas remain bound to the sorbent and are not destroyed. For this reason the modern technological processes are often equipped by the technology for the catalytic dioxins destruction.

Another efficient technology for removal of dioxins is their catalytic decomposition, occurring together with selective catalytic reduction of nitrogen oxides (SCR) by means of ammonia [Fino et al., 2003]

The reactions take place on similar types of catalysts (TiO_2, WO_3, V_2O_5) at a temperature range between 200 to 300°C and enable to reach both nitrogen oxides reduction (SCR) and dioxins destruction ($DeNO_x$/DeDiox). The installation position of combined SCR and dioxins destruction could be as *low dust* (between electrostatic precipitator-ESP and chemical cleaning in scrubber) or as a *end-of-pipe* technology (after baghouse filter and a scrubber). In the incineration plants the technology ($DeNO_x$/DeDiox) is preferably located after mechanical and chemical cleaning because especially higher heavy metals in the treated gas rapidly decrease the activity of the catalyst. The efficiency of dioxins destruction could reached up to the level approx. 98 % [2] but the sensitivity of the catalyst to the poisons and necessity of reheating cooled gas in the block of chemical cleaning back to the operation temperature is a certain disadvantage of this technology.

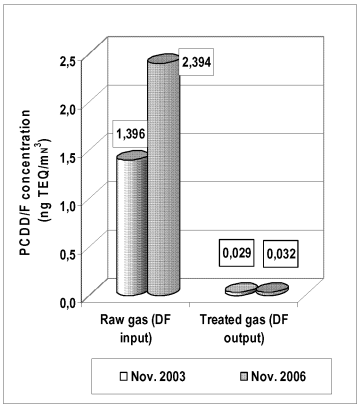
Another technological way for dioxins destruction is the technology of catalytic filtration REMEDIA™ D/F developed by company W. L. GORE & Associates, Inc. (USA). The process of REMEDIA™ D/F is an evolution of two proven technologies: catalysis and surface filtration. The system consists of an ePTFE membrane and catalytic felt substrate. The membrane, which is a GORE-TEX® membrane, captures submicron particulates, including heavy metals, without allowing particles to penetrate or pass through the catalytic felt substrate. Gaseous PCDD/Fs, however, pass through the membrane and into catalytic felt substrate. This substrate is a needle punched felt made from ePTFE fibres containing a proven dioxin-destroying catalyst. The catalytic felt destroys gaseous PCDD/Fs by means of a catalytic reaction. This technology enables both simultaneous removal of solid particles and destruction of dioxins and other persistent organic pollutants (POPs) well below the allowable limit given by environmental regulation.
As referred by Pranghofer (2001), the first commercial application of this technology was in the municipal waste incinerator IVRO in Roeselare (Belgium) in 1997 [Bonte,

2002] and still very good levels of POPs removal from flue gas are reached, without a reduction in efficiency of the original filtration material.

2. Results of operation of catalytic filtration system REMEDIA™ D/F for dioxin removal in an incineration plant

Simple application of catalytic filtration REMEDIA™ D/F based on using special filtration tubes into a classical construction fibres baghouse filter for combined flue gas cleaning, which do not need to be pre-cleaned is the main reason why this method of flue gas cleaning is becoming more widely used. At present this method of cleaning has been used in more than 50 cases on a worldwide basis in a number of technological modifications. The described advantages have been the main reasons for choosing the method of catalytic filtration REMEDIA™D/F for the extension of a block for flue gas cleaning by the so-called dioxin filter at the municipal waste incineration plant TERMIZO, Ltd., Liberec (CZ). The retrofit delivered by EVECO Brno Ltd, in October 2003 is referred to by Bebar (2005) and Piskovsky (2005).

Waste throughput of the incineration plant is 96,000 t/r (12 t/h) and about 60,000 m_N^3/h of raw flue gas which have to meet required emission limits before output are produced. Flue gas which is, after cooling down in the boiler for the production of preheated steam (HRSG), partly pre-cleaned in the ESP, is directed to the fabric dioxin filter (DF) at temperatures between 200 to 235 °C.



The results from measurements of PCDD/F concentration in the flue gas entering the dioxin filter and at DF output which were performed in 2003 and 2006 are shown in Fig. 1. They indicate that the efficiency of dioxin removal remains high during the three years operation period between 98 to 99 %. For a more detailed analysis of dioxin removal in the catalytic filter in the MSWI TERMIZO the extended measurements of concentration of toxic isomers in the raw gas, cleaned gas and separated ash have been taken. In this paper results from measurements taken in November 2006 are analysed.

Fig.1 *Results of PCDD/F measurement in the raw gas and treated gas in dioxin filter in three years period*

The analysis of samples were carried out separately to find the PCDD/F concentration in the captured particulate matter in filter of the measurement unit and in the condensate. The concentrations and mass flow of PCDD/F isomers in the gaseous stream and in adsorbed form on dust particles in the gas entering into DF and in the cleaned gas are recorded in Table 1.

Table l

The proportion and mass flow of toxic PCDD/F isomers in gaseous and adsorbed form in the raw gas and in cleaned gas

Congener		Congener concentration in the dry clean gas (ng/m_N^3)					
		Dioxin filter input			Dioxin filter output		
		gaseous form	adsorbed on particular matter	total content in the raw gas	gaseous form	adsorbed on particular matter	total content in the raw gas
PCDD toxic congeners	2,3,7,8 TCDD	0,324	0,016	0,340	0,003	0,000	0,003
	1,2,3,7,8 PeCDD	0,624	0,038	0,663	0,006	0,000	0,006
	1,2,3,4,7,8 HxCDD	0,204	0,020	0,225	0,002	0,000	0,002
	1,2,3,6,7,8HxCDD	0,246	0,041	0,287	0,006	0,000	0,006
	1,2,3,7,8,9 HxCDD	0,240	0,039	0,279	0,003	0,000	0,003
	1,2,3,4,6,7,8, HpCDD	1,080	0,594	1,675	0,035	0,003	0,038
	OCDD	1,080	2,041	3,121	0,151	0,017	0,168
	total PCDD toxic congeners	**3,800**	**2,789**	**6,589**	**0,206**	**0,020**	**0,226**
PCDF toxic congeners	2,3,7,8 TCDF	1,921	0,072	1,993	0,017	0,000	0,017
	1,2,3,7,8 PeCDF	1,561	0,144	1,705	0,030	0,000	0,030
	2,3,4,7,8 PeCDF	1,561	0,102	1,663	0,021	0,000	0,021
	1,2,3,4,7,8 HxCDF	1,561	0,162	1,723	0,030	0,000	0,030
	1,2,3,6,7,8HxCDF	1,321	0,150	1,471	0,032	0,000	0,032
	2,3,4,6,7,8HxCDF	0,084	0,019	0,103	0,002	0,000	0,002
	1,2,3,7,8,9 HxCDF	1,080	0,120	1,201	0,027	0,000	0,027
	1,2,3,4,6,7,8, HpCDF	4,322	0,840	5,162	0,082	0,003	0,085
	1,2,3,4,7,8,9 HpCDF	0,432	0,108	0,540	0,014	0,000	0,014
	OCDF	0,660	0,594	1,255	0,068	0,016	0,084
	total PCDF toxic congeners	**14,503**	**2,312**	**16,815**	**0,323**	**0,019**	**0,342**
total PCDD+PCDF toxic congeners		**18,302**	**5,102**	**23,404**	**0,529**	**0,039**	**0,568**
Equivalent toxicity							
PCDD concentration (ng TEQ/m_N^3)		0,72	0,05	0,77	0,0077	0,00004	0,0078
PCDF concentration (ng TEQ/m_N^3)		1,50	0,12	1,62	0,0236	0,00005	0,0237
PCDD/F concentration (ng TEQ/m_N^3)		**2,22**	**0,17**	**2,39**	**0,0314**	**0,00009**	**0,0315**
PCDD/F mass flow in the gas stream (μg TEQ/h)		**128,32**	**10,03**	**138,35**	**1,815**	**0,005**	**1,821**

The measured data show that the share of individual PCDD/F isomers in the gaseous form change are in relation to their molecular weight (see Fig. 2). At the dioxin filter input temperature 231 °C the octa-substituted congeners were presented in the gaseous form in only about 35 to 50 %, but tetra- to hepta-substituted derivates were presented in a much higher share, up to 95 %.

The concentration of PCDD/F in raw gas was found 2.39 ng TEQ/m_N^3 , the remaining PCDD/F concentration in cleaned gas was 0.0315 ng TEQ/m_N^3 which means reduction of dioxin toxic level to 98.7 %.

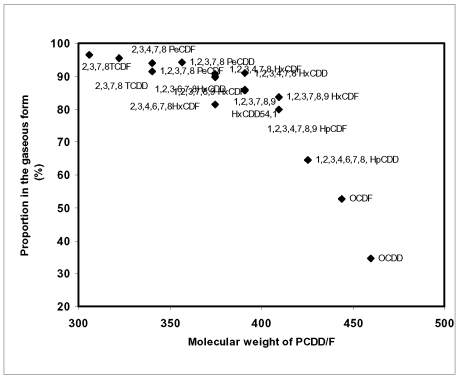


Fig. 2 *Proportion of PCDD/F isomers in gaseous form vs. their molecular weight*

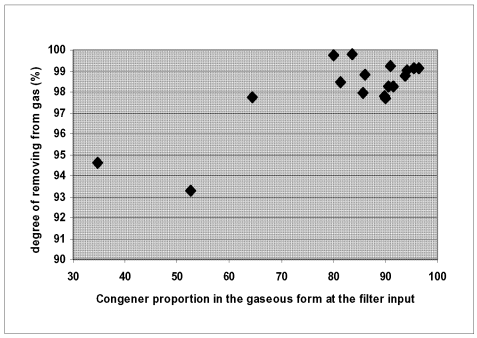


Fig. 3*: Efficiency of removing of individual PCDD/F congeners vs. their proportion in gaseous for*

Though the share of individual PCDD/F isomers in gaseous form in the raw gas was found in the region about 35 to 95 %, their degree of removing from the flue gas was higher (see Fig. 3). From the data obtained by measurements of particular matter in the gas at input and output of the dioxin filter (15.6 mg/m_N^3 and 0.5 mg/m_N^3 resp.) the average amount of separated dust in the dioxin filter was set at 0.87 kg/h. On the basis of detected concentration of toxic PCDD/F in the ash produced in dioxin filter a material balance for individual toxic congeners was calculated. We have succeeded to evaluate amount of individual decomposed PCDD/F congeners with exception of 2,3,4,6,7,8 HxCDF as it is obvious from Tab. 2.

From the total mass balance input 1352.5 μg/h of toxic congeners 73.4% was separated in the dioxin filter. Converted to toxic equivalent (TEQ) its value in cleaned gas was reduced by 98.7 % . Previous results stating that separated ash in the dioxin filter has higher level of toxicity (in this case 9.6 ng TEQ/g) were confirmed. The mass flow of PCDD/F in this ash stream was 326.3 μg/h which converted to toxic equivalent represents 8.36 ng TEQ/h corresponding to 6 % of the input value of toxicity.

Table 2 *The mass balance of individual PCDD/F congeners in the dioxin filter*

Congener	Flowrate of PCDD/F congener (μg/h)				PCDD/F decomposed	
	DF input	DF cleaned gas output	Ash from the DF	Total DF ouput	(μg/h)	(%)
2,3,7,8 TCDD	19,63	0,170	0,34	0,51	19,1	97,4
1,2,3,7,8 PeCDD	38,30	0,372	1,59	1,96	36,3	94,9
1,2,3,4,7,8 HxCDD	12,97	0,103	1,57	1,67	11,3	87,1
1,2,3,6,7,8HxCDD	16,58	0,337	4,35	4,69	11,9	71,7
1,2,3,7,8,9 HxCDD	16,13	0,190	2,42	2,61	13,5	83,8
1,2,3,4,6,7,8, HpCDD	96,78	2,179	74,12	76,30	20,5	21,2
OCDD	180,39	9,711	125,31	135,0	45,4	25,2
2,3,7,8 TCDF	115,17	0,990	1,86	2,85	112,3	97,5
1,2,3,7,8 PeCDF	98,52	1,742	3,45	5,20	93,3	94,7
2,3,4,7,8 PeCDF	96,09	1,188	4,19	5,37	90,7	94,4
1,2,3,4,7,8 HxCDF	99,56	1,742	5,48	7,22	92,3	92,7
1,2,3,6,7,8HxCDF	84,99	1,861	6,81	8,67	76,3	89,8
2,3,4,6,7,8HxCDF	5,97	0,091	10,99	11,08	-5,1	-
1,2,3,7,8,9 HxCDF	69,38	1,584	2,46	4,04	65,3	94,2
1,2,3,4,6,7,8, HpCDF	298,33	4,931	41,25	46,18	252,2	84,5
1,2,3,4,7,8,9 HpCDF	31,22	0,792	5,65	6,44	24,8	79,4
OCDF	72,50	4,859	34,44	39,30	33,2	45,8
total toxic congeners PCDD/F	1352,5	32,84	326,3	359,1	993,4	73,4

3. Conclusions

The above results and methodology can be considered as the first step in prediction of efficiency of dioxins filters in relation to various types of waste treated. The method of catalytic filtration REMEDIA™D/F applied in MSWI in TERMIZO Ltd in Liberec constantly reaches very good results in dioxin removal from flue gas created at municipal waste incineration plants. We arrived at confirming expected assumptions that various congeners are not decomposed uniformly in the dioxin filter and the stage of their decomposition depends on their representation in the gas phase. It is strongly influenced by their molecular weight.

Acknowledgements

We gratefully acknowledge financial support of the Ministry of Education, youth and sports of the Czech Republic within the framework of research plan No. MSM 0021630502 „Waste and Biomass Utilization focused on Environmental Projection and Energy Generation“ as well as support from the Czech Science Foundation within project No. OE 156.

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