



## Combined Flue Gas Cleaning from Persistent Organic Compounds and Nitrogen Oxides in the Multifunction Filter

Filip Jedlička<sup>a</sup>, David Jecha<sup>\*a</sup>, Ladislav Bébar<sup>a</sup>, Jaroslav Oral<sup>b</sup>, Petr Stehlík<sup>a</sup>

<sup>a</sup>Brno University of Technology, Institute of Process and Environmental Engineering, Technická 2896/2, 616 69 Brno, Czech Republic

<sup>b</sup>EVECO Brno, s.r.o., Březinova 42, 616 00 Brno, Czech Republic  
[jedlicka@upei.fme.vutbr.cz](mailto:jedlicka@upei.fme.vutbr.cz)

Production of new products is associated with the generation of waste that must be processed in some way. Besides recycling, as another opportunity to processing waste, there is the possibility of energetic utilization. Combustion of waste creates many pollutants that are hazardous for the environment. Pollutants, mainly nitrogen oxides (NO<sub>x</sub>), persistent organic compounds and acidic gases (SO<sub>x</sub>, HF, HCl) produced during combustion can be removed using various methods, generally comprising multiple individual devices. The 4D filtration technology can reduce the above mentioned pollutants in one device, respectively in the filter, containing catalytically active fabric bags or ceramic candles. Observations focused on reducing NO<sub>x</sub> were carried out in the industrial wastes incineration plant that was implemented by EVECO Brno, s.r.o. The filter is equipped with ceramic tubes of Clear Edge Filtration® using a multi-filtration technology, called 4D filtration. The results of operational tests focused on reducing the NO<sub>x</sub> concentration by adding aqueous ammonia solution into the flue gas stream in front of the ceramic filter will be presented.

The paper presents also the results of an operation test performed on municipal solid waste incineration plant (MSWI) where cleaning of gaseous combustion products from persistent organic pollutants is achieved by the technology of catalytic filtration REMEDIA™ D/F. During this operation test which was performed with the W.L.GORE, GmbH, there were carried out measurement in two regimes, differing in size of dosage of ammonia aqueous solution into the flue gas stream in order to achieve non-catalytic reduction of nitrogen oxides (SNCR). In the test was monitored the content of particular toxic polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/F), certain polyaromatic carbohydrons (PAH) and polychlorinated phenols (PCB), in total called persistent organic pollutants (POPs), in flue gas on the catalytic filter outlet and inlet. The efficiency of removing monitored harmful substances was slightly lower in the regime with higher ammonia dosage.

### 1. Operating experiment in hazardous waste incinerator SPORTEN a.s.

In Nove Mesto na Morave is located a leading Czech producer of ski and snowboard company Sporten a.s. During the production process creates a waste of good heating value that the company destroyed in internal waste incinerator. The incinerator is also designed for disposal waste from a nearby hospital. The hazardous waste incinerator for the processing output of 150 kg/h consists of a pyrolysis furnace, afterburner chamber, steam boilers, flue gas cleaning system (dry sorption reactor, catalytic filter, wet scrubber) and other support facilities (such as flue gas cooler, fans, dispenser sorbent, etc.). Originally

Please cite this article as: Jedlička F., Jecha D., Bébar L., Oral J. and Stehlík P., (2012), Combined flue gas cleaning from persistent organic compounds and nitrogen oxides in the multifunction filter, Chemical Engineering Transactions, 29, 1063-1068

there was installed a common fabric filter for capture particulate substance and in wet scrubber there was a reduction of gaseous pollutants. In 2010, at the end of life of the filter fabric, the company EVECO Brno Ltd. designed and implemented a new filtration device that is equipped with ceramic filter elements with integrated catalyst from Clear Edge Filtration ®. Ceramic filter elements are specially designed for the filtration technology, called 4D filtration, where one device can remove dust, POPs (persistent organic pollutants), nitrogen oxides (NO<sub>x</sub>) and acidic gases (SO<sub>2</sub>, HCl, HF). The last group of named pollutants are mainly reduced in the reactor before filtration equipment. In the incinerator is applied only three "D" of 4D filtering - DeDusting, DrySorption and DeDiox. DeNO<sub>x</sub> is not carried out because incineration safely comply daily emission limit of current legislation, which is for existing equipment 400 mg NO<sub>2</sub>/m<sub>N</sub><sup>3</sup>.

On April 25, 2012 operational test was carried out with a focus on the disposal of NO<sub>x</sub> selective catalytic reduction. The aim of the experiment was to determine whether it is possible to reduce NO<sub>x</sub> emissions to the applicable emission limit of 200 mg/m<sub>N</sub><sup>3</sup> valid for new incinerators and incineration plants with a nominal capacity 6 t/h. The test consisted in the injection 25 % aqueous solution of NH<sub>3</sub>, which serves as a reducing agent for SCR NO<sub>x</sub> (EIPPCB, 2009). At the same time there was dosed NaHCO<sub>3</sub> sorbent to the reactor for reducing acid gas components. The reducing agent was dosed into the pipe by a pump through the heating tube, which was an aqueous solution of NH<sub>3</sub> evaporation. Ammonia is then automatic sucked into flue gas pipe, because in the system before the filter is negative pressure.

In the first phase of the test was set dosing ratio NH<sub>3</sub>: NO = 0.9, which corresponded to the dosage to 1.0 liter of ammonia per hour. At this molar ratio there measured approximately 4 hours and then increased the dosage of ammonia to 1.5 L/h, which corresponded to the molar ratio NH<sub>3</sub>: NO = 1.4. The initial concentration of NO<sub>x</sub> was changing during the experiment, but the amount of dosing reducing agent remained for the setting value constant. The molar ratios correspond of the median of all measured input concentrations of NO, 115 mg/m<sub>N</sub><sup>3</sup>.

Sampling sites for flue gas analysis was located in the flue pipe just before the filter and the other filter, near the chimney fan. Reaction temperature measured before the filter was almost constant, its average value was 178 °C.

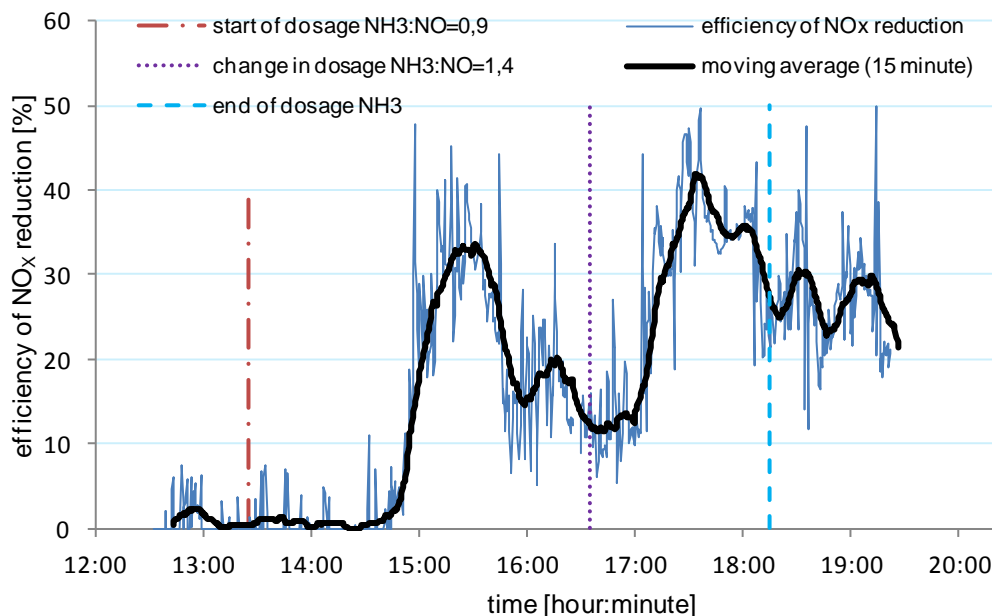


Figure 1: The course of disposal efficiency of NO<sub>x</sub> during the experiment

Measurement began at 12:30 with no dosage of ammonia. Although SCR NO<sub>x</sub> did not proceed, it was observed a reduction of NO<sub>x</sub> emissions (see Figure 1). This effect is caused by reaction NO<sub>x</sub> with

NaHCO<sub>3</sub> and NO<sub>x</sub> removal efficiency reaches up to 10 % depending on operating conditions (Kong, Davidson, 2010). At the beginning of dosage of ammonia at a molar ratio of 0.9 remained level efficiency NO<sub>x</sub> reduction unchanged. Approximately after 1.5 h was active sites of catalyst saturated by ammonia and SCR NO<sub>x</sub> began take place. In the graph in Figure 2 can be observed emission peaks which are due to the discontinuous dosage of waste (about twice per hour). At the peak NO<sub>x</sub> SCR achieves the highest efficiency. The average removal efficiency NO<sub>x</sub> achieved 20 % at ratio NH<sub>3</sub>: NO = 0.9 mol/mol. After increasing the dosage of reducing agent (NH<sub>3</sub>: NO = 1.4) NO<sub>x</sub> removal efficiency was 30 %. The experiment also included a sampling flue gas behind the filter to detect NH<sub>3</sub> slip at both molar ratios. For both samples was not detected any ammonia slip at a given accuracy (<0.10 mg/sample). Due to the low operating temperature and the reaction stoichiometry can be expected that further increasing the molar ratio will not have a significant effect on efficiency of NO<sub>x</sub> disposal. It could also lead to emissions of ammonia, NH<sub>3</sub> slip.

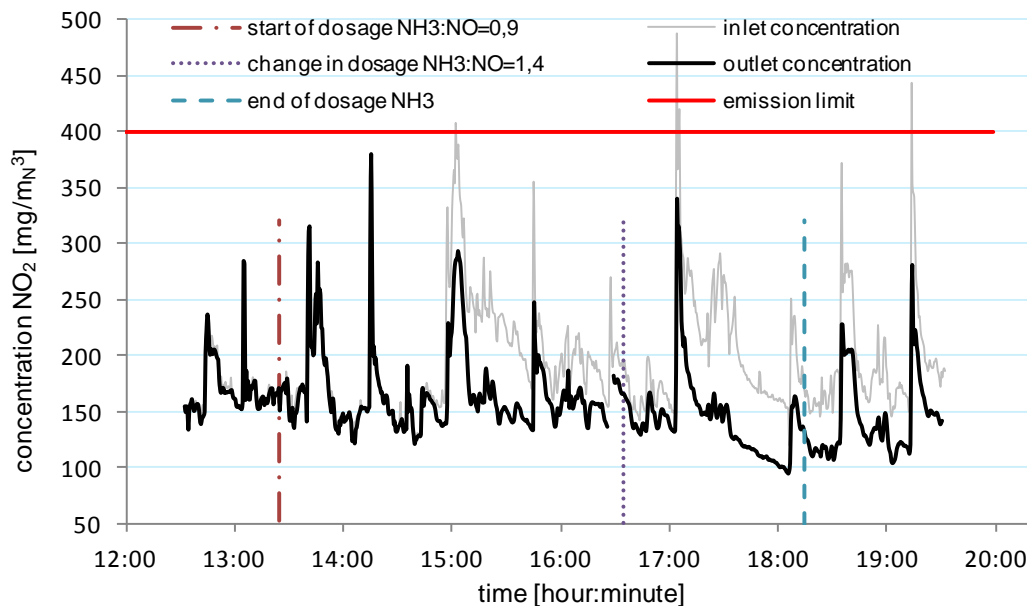


Figure 2: The course of the input and output concentrations of NO<sub>x</sub> of 4D filter

## 2. Operating experiment in MSWI TERMIZO

In 2003 in Municipal Solid Waste Incineration TERMIZO (MSWI) in Liberec (CZ), the process of flue gas cleaning was extended with REMEDIA™ D/F catalytic filtration technology with W. L. GORE & Associates, Inc. (USA). Realization and integration of the technology was carried out by EVECO Brno, s.r.o.. Technology of catalytic filtration allows for efficient combined elimination of solid substances and catalytic decomposition of POPs from gaseous exhalation to the level well below emission limit 0.1 ng TEQ/mN<sup>3</sup> stipulated by EU and Czech legislation. Principle of this technology consists of application of special textile for filtration bags of textile filter where particles of fine ash are efficiently removed while dioxins presented in the filtered gas are decomposed. Filtration material is made of two layers of expanded polytetrafluorethylene (ePTFE) with inside layer containing implemented catalytic component efficient in dioxin decomposition.

In April 2010 in MSWI TERMIZO, all filtration bags in dioxin filter were replaced after having been in service for 6 and half year (since October 2003) and having processed over 600,000 t of waste. Technology supplier W.L.GORE & Associates, GmbH Company utilized final phase of filtration bags operation for operational experiment focused on impact assessment of increased ammonia concentration upon properties of special multifunctional filtration material and for monitoring of impact

of increased ammonia concentration upon additional degree of nitrogen oxides in dioxin filter. Operational experiment was organized by W. L. GORE & Associates, GmbH, Putzbrunn-München and report on results of NO<sub>x</sub> elimination was written. Institute of Process and Environmental Engineering at Brno University of Technology joined the experiment pursuing to assess impact of increased ammonia concentration upon efficiency of elimination of substances from POPs group.

Objective of the operational test was to assess whether intentionally increased ammonia concentration in flue gas entering dioxin filter may increase additional reduction of nitrogen oxides. Operating mode of Incinerator was stable during all the experiment. It processed 12 (t waste)/h and temperature at the inlet to the dioxin filter was 220 ° C. In regular operational conditions at MSWI TERMIZO, 50 to 60 L/h of solution containing 25 % NH<sub>4</sub>OH is dosed and applying process of non-catalytic reduction of nitrogen oxides (SNCR) leads to decrease of NO<sub>x</sub> content to the level of ca. 160 to 180 mg NO<sub>2</sub>/m<sub>N</sub><sup>3</sup>. This level well complies with emission limit for nitrogen oxides (which is 200 mg NO<sub>2</sub>/m<sub>N</sub><sup>3</sup>) formed in waste incinerators processing more than 6 t/h. Given dosing of ammonia solution corresponds to NH<sub>3</sub>/NO ratio of ca. 1.4 to 1.6 mol/mol before SNCR process for expected concentration of flue gas released from combustion space at level of 350 mg NO<sub>2</sub>/m<sub>N</sub><sup>3</sup>. However, it is necessary to point out the fact that measuring of dosed amount of ammonia solution at the said apparatus is rather unreliable.

Increase of ammonia solution dosing was carried out via setting the required concentration of NO<sub>2</sub> in final flue gas, this lead to residual concentration of NO<sub>x</sub> to the level of 25 mg NO<sub>2</sub>/m<sub>N</sub><sup>3</sup> with NH<sub>3</sub>/NO ratio of 3.25 mol/mol before SNCR, i.e. double value in contrast to the value in regular situation. Mutual relation between achieved nitrogen oxides concentration in final flue gas and NH<sub>3</sub>/NO ratio at the area of injection of ammonia agent into boiler is presented in Figure 3; it clearly shows that even non-catalytic method allows for NO<sub>x</sub> concentrations in flue gas below 100 mg NO<sub>2</sub>/m<sub>N</sub><sup>3</sup>.

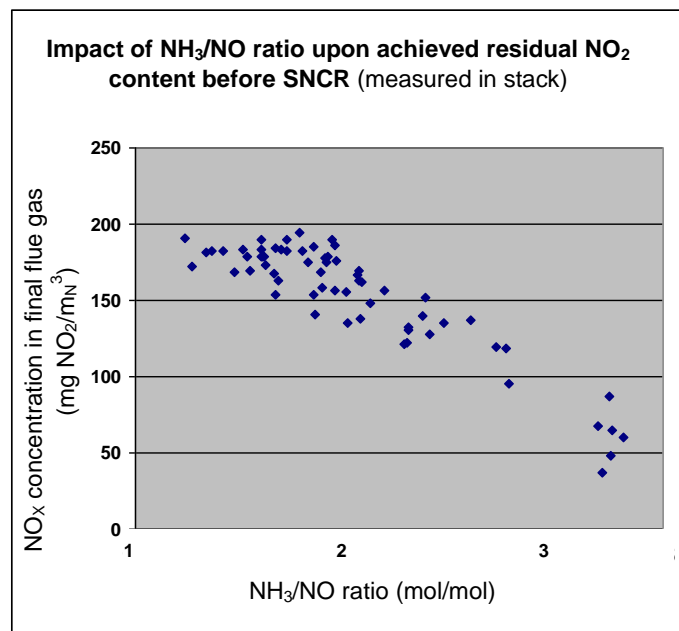


Figure 3: Impact of NH<sub>3</sub>/NO ratio before SNCR upon achieved residual content of NO<sub>2</sub> in final flue gas

Results of measuring of NO<sub>x</sub> concentration in flue gas at measuring points at inlet and outlet to/from filter were processed by W.L.GORE, GmbH and it proved that certain decrease of nitrogen oxides content occurs in textile filter set up with filtration material and implemented catalytic component efficient in dioxin decomposition. Analysis showed that nitrogen oxides concentration decreased by 12 to 30 mg NO<sub>2</sub>/m<sub>N</sub><sup>3</sup> in fabric filter depending on amount of dosing of ammonia solution.

Increase in dosing of ammonia agent into flue gas is accompanied with increase in residual content of ammonia in flue gas after non-catalytic reduction of nitrogen oxides. This assumption was not proved in

measuring of  $\text{NH}_3$  concentrations at place before filter and ammonia concentration at the inlet according to results conducted by mobile analyzer at dioxin filter ranged up to  $2 \text{ mg NH}_3/\text{m}_\text{N}^3$ . Authors then assume that results of measuring of  $\text{NH}_3$  concentration in flue gas cannot be provable for this test since operational experience, e.g. at SAKO Brno incinerator (Dvořák, 2011), proves that residual content of  $\text{NH}_3$  reaches up to  $50 \text{ mg}/\text{m}_\text{N}^3$  for increased dosing of ammonia agent into flue gas for increase of SNCR process efficiency.

As stated above, with increased dosing of ammonia agent into combustion products in the area of the boiler, it is necessary to expect also the increase of residual content of ammonia in the combustion products entering the dioxin filter. Because used catalytic contacts for selective reduction of nitrogen oxides (SRC) and for catalytic decomposition of dioxins are quite similar and usually use  $\text{TiO}_2$ ,  $\text{WO}_3$  or  $\text{V}_2\text{O}_5$  oxides, there was assumed possible inhibition of the reaction of catalytic decomposition of dioxins in presence of  $\text{NH}_3$  and  $\text{NO}$  in cleaned combustion products in the dioxin filter embedded with filtration material with implemented catalyst for the catalytic filtration technology REMEDIA™ D/F. Given that persistent organic substances occur in cleaned gas in concentrations on the „ $\text{ng}/\text{m}_\text{N}^3$ “ level, the increased concentration of  $\text{NH}_3$ , albeit in units of „ $\text{mg}/\text{m}_\text{N}^3$ “, could lead to certain influencing of efficiency of elimination of POP group substances.

To verify this assumption there were performed simultaneous samplings of combustion products by authorized measuring group in front of dioxin filter and stack in order to determine the content of the POPs group substances, in two modes varying in the amount of dosing of ammonia agent in the combustion products.

In the mode I (dosage of ammonia for SNCR in the ratio of  $\text{NH}_3:\text{NO} = 1.61 \text{ mol}/\text{mol}$ ) the total input concentration of toxic PCDD/F was  $10.70 \text{ ng}/\text{m}_\text{N}^3$ , which corresponds to the concentration of  $1.207 \text{ ngTEQ}/\text{m}_\text{N}^3$  after recalculation to toxic equivalent. In the mode II ( $\text{NH}_3:\text{NO} = 3.25 \text{ mol}/\text{mol}$ ) the total input concentration of toxic PCDD/F was  $16.80 \text{ ng}/\text{m}_\text{N}^3$ , which corresponds the concentration of  $1.653 \text{ ngTEQ}/\text{m}_\text{N}^3$  after recalculation to toxic equivalent. The concentration of PCDD/F in the output combustion products in the mode I was  $0.0121 \text{ ngTEQ}/\text{m}_\text{N}^3$ , which corresponds to approximately eightfold allowance in relation to the valid emission limit. The concentration of PCDD/F in the output combustion products in the mode II was  $0.0483 \text{ ngTEQ}/\text{m}_\text{N}^3$ , which corresponds to approximately double allowance in relation to valid emission limits. A graphic comparison of total concentration of PCDD/F in output combustion products in operation modes differing by the dosing amount of the ammonia solution is depicted in Figure 4.

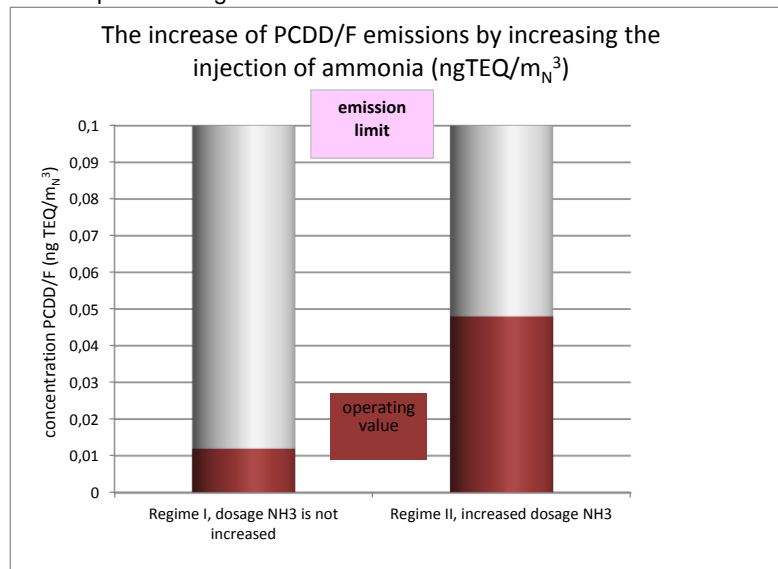


Figure 4: A comparison of total concentration of PCDD/F in output flue gas in operation modes differing by the dosing amount of the ammonia solution

While in the mode I the total degree of PCDD/F elimination was 99 % and the degree of elimination of particular congeners ranged from 96 to 99 %, in the mode II with higher dosing of ammonia solution the total degree of elimination of dioxins decreased to 97.3 % and the degree of elimination of particular congeners ranged from 94 to 98 %. Even this small change in efficiency decline of dioxin filter on the PCDD/F group substances elimination was expressed by quadruple increase of the residual concentration of PCDD/F in output combustion products. But it is important to keep in mind that in the mode II the input concentration of dioxins in the combustion products entering the dioxin filter was about 60 % higher.

Similar results were also observed for PAH, where the removal efficiency decreased by 5.6 % and 6.3 % for PCPh (Jedlička, 2011).

### 3. Conclusion

Operating experiment in incinerator of hazardous waste Sporten a.s Nové Město na Moravě was focused on reducing NO<sub>x</sub> from the flue gas with catalytically active ceramic filtration elements. During the experiment was carried out a complete 4D filtration, namely DeDusting, DrySorption, DeDiox and DeNO<sub>x</sub>. NO<sub>x</sub> destruction efficiency ranged between 15 % and 40 % depending on the input NO<sub>x</sub> concentration and molar ratio of NH<sub>3</sub>: NO. In the first part of the test was the molar ratio NH<sub>3</sub>: NO = 0.9 and corresponding average efficiency NO<sub>x</sub> reduction was 20 %. At increased dosage reducing agent (NH<sub>3</sub>: NO = 1.4) was achieved 30 % of efficiency NO<sub>x</sub> reduction.

The operational experiment in the MSWI TERMIZO Liberec took place in modes differing in the amount of dosing of aqueous ammonia solution into combustion products. The results show that in the mode with increased dosing of ammonia solution in all of the three groups of observed persistent organic substances a certain decrease of aggregative degree of elimination of particular groups of these compounds was reached; in case of the PCDD/F group by 1.7 %, in case of polyaromatic compounds by 5.6 % and in case of polychlorinated phenols by 6.3 %. Although the decrease in the degree of elimination in case of the PCDD/F group was quite low, this little change in the decrease of efficiency of the dioxin filter resulted in quadruple increase of concentration of PCDD/F in output combustion products and in reaching approximately 50 % of the value of the emission limit for this group of substances. So, from the point of view of permanent adherence to emission limit of PCDD/F the overdose of ammonia into the combustion products flow in order to DeNO<sub>x</sub> can be connected with certain risk. The findings about different degree of dioxins elimination in modes differing in the amount of dosing the ammonia solution, although these are findings from one-time measurement, support the opinion that in the environment with increased content of NH<sub>3</sub> the reaction of catalytic decomposition of the PCDD/F substances group might be suppressed to some degree.

### References

- Czech Government Regulation No. 354/2002  
Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste, Official Journal of the European Communities ,28.12.2000, Brussels, Belgium  
Dvořák R., Hanák R., Jedlička F., Bébar L., 2011, Zneškodňování NO<sub>x</sub> pomocí katalytické filtrace. Odpadové fórum, <[www.odpadoveforum.cz](http://www.odpadoveforum.cz)> accessed 13.4.2011.  
European IPPC Bureau. Reference Document on the Best Available Techniques for Large combustion plants, Brussels, <[eippcb.jrc.es](http://eippcb.jrc.es), 2009>, accessed 01.08.2012  
Jedlička F., Hanák L., Bébar L., 2011, Provozní experiment kombinovaného čištění spalin od persistentních organických látek a NO<sub>x</sub> v dioxinovém filtru, CHISA 2011, pp.91-110, ISBN 978-80-905035-0-2.  
Kong Y., Davidson H., 2010, Dry sorbent injection of sodium sorbents for SO<sub>2</sub>, HCl and mercury mitigation, Orlando, <[www.seas.columbia.edu](http://www.seas.columbia.edu)> accessed 11.5.2010.