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# New approach to common removal of dioxins and NOx as a contribution to environmental protection

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#### ABSTRACT

Meeting environmental limits represents the most important issue in the field of waste processing. Our primary effort consists either in eliminating hazardous emissions or in prevention of their production. However, this is not feasible in most cases therefore the so called secondary methods have to be applied. Technologies based on adsorption of hazardous compounds using activated carbon, deNOX/ deDiox technologies as well as technology of catalytic filtration using a special material REMEDIA<sup>®</sup> proved itself to be very efficient. The latter technology consists in using a baghouse with bags manufactured from a special material (two layers – membrane from ePTFE and felt with bound in catalyst) called REMEDIA<sup>®</sup> which has successfully been used for removal of PCDD/F during recent period. However, it has been found that this technology can partially remove NOx as well. Based on our experience from operation industrial incineration plants it has been proved that even after more than three years' operation the activity of filtration material was not decreased and efficiency of dioxins removal from flue gas ranges from 97 to 99% (Pařízek et al., 2008).

Based on industrial experience and new findings it has been decided to focus continuing research and development on deNOx experiments by applying SCR using the above mentioned efficient filtration material. This type of material is primarily designed for reduction of PMs and PCDD/F. Experiments with this filtration material should test possibilities for simultaneous reduction of PMs, PCDD/F and NOx. Tests are performed in MSW incineration plant utilizing new experimental unit and under standard conditions. Waste processing capacity of the incineration plant amounts to 15 t/h. Tests result in evaluation of overall reduction efficiency and negative factors that might influence the efficiency. Catalytic filtration is further compared to other types of deNOx methods.

Thus we have obtained qualitatively new knowledge about this method the value of which is emphasized by full scale industrial testing.

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#### 1. Introduction

New European Union regulations (Council Directive 2000/76/ EC, 2000) as well as other ones worldwide have resulted in more stringent environmental limits for all pollutants originating

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during the thermal processing of various types of waste. Ways of how to achieve energy reduction and consequently emissions reduction are discussed by Dovì et al. (2009). Regulations require that hazardous components have to be efficiently removed before they enter the ambient (Council Directive 2000/76/EC, 2000). 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 MSW and industrial waste are PCDD/F.

However, NOx also represent a serious issue. If a general fuel is considered, combustion of  $N_2$  instigates its reaction with oxidant, i.e. with auxiliary combustion air which contains approximately 78% of  $N_2$ . Combustion forms NOx mostly represented by nitric oxide (NO) and partially by nitrogen dioxide (NO<sub>2</sub>), there may also





Abbreviations: deDiox, removal of dioxins; deNOx, removal of NOx; ePTFE, expanded polytetrafluorethylen; ESP, electrostatic precipitator; GORE-TEX<sup>®</sup>, special fabrics from W. L. Gore & Associates, Inc.; MSW, municipal solid waste; NOx, nitrogen oxides; PCDD/F, polychlorinated dibenzo-p-dioxins and furans (also know as "dioxins"); PMs, particulate matters; REMEDIA<sup>®</sup>, catalytic filtration system from W. L. Gore & Associates, Inc.; SCR, selective catalytic reduction of NOx; SNCR, selective non-catalytic reduction of NOx; VOCs, volatile organic compounds.

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be nitrous oxide (N<sub>2</sub>O) present. NO is colorless toxic gas which quickly reacts with oxygen (O<sub>2</sub>) in the atmosphere to form NO<sub>2</sub>. Legislation then usually expresses NOx concentration as NO<sub>2</sub> concentration. NO and NO<sub>2</sub> in the atmosphere create undesired ozone in lower atmosphere (which is desired in the upper atmosphere) as well as smog and acid rain, where NO<sub>2</sub> reacts with water (H<sub>2</sub>O) and forms acids such as nitrous acid (HNO<sub>2</sub>) and nitric acid (HNO<sub>3</sub>).

Amount of formed NOx is influenced by several factors such as temperature of combustion, flow velocity in combustion space, combustion space design, burner design, fuel composition, ratio of fuel and air dosage, heat removal rate from combustion space, etc. (Baukal, 2004).

Methods of NOx control may be categorized into primary methods which prevent formation of NOx; secondary NOx control methods which effectively reduce already formed NOx. Among the primary methods there are (Baukal, 2004):

- usage of fuel with low nitrogen content,
- usage of fuel additives,
- pretreatment of fuel,
- usage of different oxidant (with lower nitrogen content),
- reduction preheating of added air,
- reduction air excess,
- distribution fuel dosing into several steps (staging),
- flue gas recirculation,
- water/steam dosage,
- auxiliary dosage of different fuel for reduction of NOx formation,
- low NOx burners,
- and others.

Primary methods may be successfully used in the so called clean applications where only fuels are combusted, e.g. for preheating of other types of media, etc. However, their efficiency is limited when it comes to heterogeneous waste. This type of waste requires secondary methods for deNOx. Among the most common secondary deNOx methods there are (Heck et al., 2002; European IPPC Bureau, 2008a):

- selective non-catalytic reduction of NOx (SNCR),
- selective catalytic reduction of NOx (SCR) depending on the catalyst used, there are SCR technologies utilizing fixed-bed catalytic reactor and technologies with catalyst applied on fabric or ceramic filter (the so called catalytic filtration), technologies with fluidized bed are not very common,
- flue gas cleaning using NOx absorption (Dalaouti and Seferlis, 2005).

All these methods may be combined, which increases efficiency of NOx reduction as well as NOx formation. Selection of individual method or combination of methods is always conditioned by economic balances and legislation.

Based on literature sources and previous experience any contribution bringing an added value, and/or a novel approach to deNOx/ deDiox system is valuable.

We will now focus on following technologies.

1.1. Combined selective catalytic reduction of NOx (SCR) and dioxins destruction

Efficient technology for removal of dioxins is their catalytic decomposition, occurring together with SCR by means of ammonia (NH<sub>3</sub>) (Fino et al., 2003) according to the following stoichiometric equations:

$$4NO + 4NH_3 + O_2 \to 4N_2 + 6H_2O$$
 (1)

$$C_{12}H_nCl_{8-n}O_2 + (9+0.5n)O_2 \rightarrow (n-4)H_2O$$
  
+ 12CO<sub>2</sub> + (8 - n)HCl (2)

The reactions leading to the concurrent destruction of both NOx and dioxins (deNOx/deDiox) proceed in a catalytic reactor at temperature interval from approximately 200 to 300 °C (Goemans et al., 2003). The efficiency of destruction of NOx is high in the catalytic reactor but the reactor has also a certain disadvantage in its sensitivity to catalytic poisons and in a necessity to include it into the technology line only at a point where the flue gas is free of PMs which practically means after mechanical and chemical cleaning.

This configuration requires reheating of flue gas up to the temperature necessary for reactions taking place in the deNOx/ deDiox reactor (see Fig. 1).

#### 1.2. Catalytic filtration

Based on evaluation of applications it has been found that the method of dioxin removal by catalytic filtration REMEDIA® (Pranghofer and Fritsky, 2001; Bonte et al., 2002) is still highly effective even after long time of operation, which considerably reduces the total annual cost. The method of catalytic filtration is based on a special GORE-TEX<sup>®</sup> material which is used for the filtration bags of the fabric filter, where solid matters of fly ash are successfully separated and at the same time dioxins present in the filtered gas are broken down. The outer filter layer which is made out of a membrane from ePTFE, can separate up to 96.6% of fly ash particles also containing compounds of heavy metals in the filtered gas. The cleaned gas enters the inner layer of the filtration layer which has in its structure built in components acting as catalysts breaking down dioxins with 98.8% efficiency (at a level from 0.01 to  $0.03 \text{ ng TEQ/N m}^3$ ). The filtration material is cleaned by a pulse-jet cleaning method.

The implemented alternative of flue gas cleaning technology at the incineration plant in question is obvious from Fig. 2.

When testing efficiency of PCDD/F reduction in the above mentioned MSW incineration plant (maximum waste processing



Fig. 1. Scheme of deNOx/deDiox technology (Pařízek et al., 2008).



Fig. 2. Scheme of MSW incineration plant with installed catalytic filter.

capacity of 15 t/h and flue gas production of  $65,000 \text{ N m}^3/\text{h}$ ) using SNCR method for NOx reduction, it was discovered that residual NOx reacts with residual ammonia in the above mentioned filtration material, which further lowers NOx concentration.

Catalytic filter in this test is positioned in between ESP and wet scrubber of flue gas. Residual ammonia does not interfere with structure of filtration material and even lowers amount of NOx in flue gas; more tests could be then performed to find out deNOx efficiency under various conditions.

Reduction of NOx by applying SCR method is usually done in temperatures ranging from 175 to 600 °C depending on type of catalyst (Heck et al., 2002). REMEDIA<sup>®</sup> filtration material should work in temperature conditions ranging from 220 to 240 °C (Smejkal et al., 2009). Key feature of SCR technology is the injection of NH<sub>2</sub>-X compounds (X being H, CN or CONH<sub>2</sub>) into gas stream (flue gas stream) (European IPPC Bureau, 2008a). Consequently, NOx is reduced to nitrogen (N<sub>2</sub>) and water (H<sub>2</sub>O) at catalyst (principle of catalytic filtration is displayed at Fig. 3). Most common reaction agent is ammonia water (NH<sub>4</sub>OH, water solution of



Fig. 3. Principle of decomposition of NOx at catalytic filter.

ammonia) or pure ammonia. Among other types of reaction agents there are urea solutions, nitrolime and cyanamide (European IPPC Bureau, 2008a). Catalysts involve noble metals such as  $Pt/\chi$ -Al<sub>2</sub>O<sub>3</sub>, compounds such as V2O5/TiO2, V2O5-WO3/TiO2, V2O5-MOO3/TiO2, MnOx/CeO<sub>2</sub>, Rh<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub> or zeolites (Fino et al., 2004). V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/ TiO<sub>2</sub> catalyst for REMEDIA<sup>®</sup> filtration material is located on ePTFE layer (Weber et al., 2001). ePTFE shows high resistance to most types of loading such as chemical, thermal, UV attack as well as good abrasion resistance; it also does not absorb water. Filtration material is covered with membrane which captures PMs. This reduces the amount of PMs in flue gas and also protects catalytic laver from fouling. Catalytic filtration requires specific filter (baghouse) design which allows reaching  $0.8-1.4 \text{ m}^3/\text{m}^2$ .min of filtration velocity (European IPPC Bureau, 2008a), Decomposition of NOx requires over-stoichiometric amount of NH<sub>3</sub>, optimum ratio is  $NH_3:NO = up$  to 1.1 mol/mol (European IPPC Bureau, 2008a). Decomposition of NOx gives rise to desired reactions (see (3)-(9)) which reduce the amount of NOx; however it also gives rise to parallel undesired reactions (10)-(13) which increase the amount of NOx or which may reduce amount of reaction agents necessary for the reaction.

Desired reactions of NOx with NH<sub>3</sub> (Schnelle and Brown, 2001):

$$4NO + 4NH_3 + O_2 \to 4N_2 + 6H_2O$$
(3)

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$$
 (4)

$$2NO_2 + 4NH_3 + O_2 \to 3N_2 + 6H_2O$$
 (5)

$$6NO_2 + 8NH_3 \to 7N_2 + 12H_2O \tag{6}$$

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$$
 (7)

Desired reactions of NOx with urea solution/(NH<sub>2</sub>)<sub>2</sub>CO/ (European IPPC Bureau, 2008b):

$$4NO + 2(NH_2)_2CO + 2H_2O + O_2 \rightarrow 4N_2 + 6H_2O + 2CO_2$$
(8)

$$6NO_2 + 4(NH_2)_2CO + 4H_2O \rightarrow 7N_2 + 12H_2O + 4CO_2$$
(9)

Undesired reactions (Busca et al., 1998):

$$4NH_3 + 3O_2 \to 2N_2 + 6H_2O \tag{10}$$

 $2NH_3 + 2O_2 \to N_2O + 3H_2O \tag{11}$ 

$$4NH_3 + 5O_2 \to 4NO + 6H_2O$$
 (12)

 $4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O \tag{13}$ 

Following authors have recently dealt with the issue of NOx elimination from flue gas or waste gas stream by catalytic filtration method: Nacken et al. (2007) and Heidenreich et al. (2008) have discussed possibilities of using  $V_2O_5$ –WO<sub>3</sub>/TiO<sub>2</sub> catalyst located in ceramic filtration element. Laboratory tests of the filtration element then showed up to 96% deNOx efficiency with optimum temperature at 300 °C. Kim et al. (2007) have also dealt with usage of modified  $V_2O_5$ –WO<sub>3</sub>/TiO<sub>2</sub> catalyst.

Kang et al. (2009) have used MnOx catalyst in a filter which results in subsequent 92.6% deNOx efficiency and temperature of 150 °C. Park et al. (2009) have incorporated an adjusted CuMnOx catalyst in a ceramic filter. Laboratory tests then showed up to 94% deNOx efficiency with temperature of 200 °C.

Zürcher et al. (2008) have researched possibilities of kinetics of deNOx in catalytic filters and Döring et al. (2008) have discussed impact of filtration velocity on deNOx efficiency at catalytically impregnated filtration elements; he has also described dependency of this reduction on various operational conditions.

#### 2. Experimental unit

Tests of efficiency of REMEDIA<sup>®</sup> filtration material are performed using new experimental unit which utilizes various technologies (Stehlík, 2009) and enables to clean pollutants in waste gas (flue gas) produced in real operations (especially in MSW and hazardous waste incineration plants). Some of the pollutants are:

- particulate matters (PMs),
- inorganic compounds (HCl, HF) and sulphur dioxide (SO<sub>2</sub>),
- volatile organic compounds (VOCs),
- polychlorinated dibenzo-p-dioxins and furans (PCDD/F),
- nitrogen oxides (NOx),
- heavy metals.

Experimental unit flexibly uses technologies such as filtration, catalytic filtration, adsorption, dry flue gas cleaning and catalytic decomposition of pollutants in order to clean these substances.

The whole experimental unit is designed to process  $1000 \text{ m}^3/\text{h}$  of waste gas (flue gas) with maximum temperature of  $250 \,^{\circ}\text{C}$  and may be connected to technology with underpressure reaching 10 kPa. Design of the unit is quite unique. Most important feature of the unit is its mobility; unit may be transported and installed right at the facility. Thus the whole unit is a separate and self-sufficient entity except for power (400 V/63 A) and water supply. Unit is composed of several parts, see following chapters (3D model of the unit is displayed in Fig. 4).

#### 2.1. Filter (baghouse)

This part consists of the filter itself, hopper and structural steel. Capture/disposal of PMs, NOx and PCDD/F using filtration and/or catalytic filtration may be tested here. Filter itself consists of fifteen filtration bags with 152 mm diameter and 2500 mm length. This arrangement leads to filtration area of  $17.9 \text{ m}^2$  and corresponding filtration velocity of  $0.93 \text{ m}^3/\text{m}^2$ min. Filter design meets

requirements on filtration velocity of  $1.0 \text{ m}^3/\text{m}^2$ .min considering processing of  $1000 \text{ m}^3/\text{h}$ . Regeneration of filtration bag is performed by usage of compressed air pulse-jet cleaning.

Overall pressure loss of the filter is considered to be at most 2 kPa for highest load, i.e. for 2 g/m<sup>3</sup> of PMs content and flue gas flow rate of 1000 m<sup>3</sup>/h. Calculated pressure loss of filtration bags is then approximately 1.4 kPa and pressure loss of the filter itself reaches 0.2 kPa (chambers, etc.).

#### 2.2. Replaceable side modules (adsorption/SCR modules)

There are two alterable modules located on the side of the filter. These modules may be altered for the purposes of adsorption cleaning of waste gas or they may contain packed catalyst for SCR.

Flow rate velocity is a key factor in design of the adsorption modules; the velocity for active carbon may range from 0.1 to 0.5 m/s with 0.5 m high layer. Height of active carbon layer required is 0.25 m which is reflected in 0.1 m/s velocity (smaller height of layer is selected because of the need for compactness of the whole experimental unit). Adsorption area is  $2.8 \text{ m}^2$ ; after the adsorption module is designed, the area is enlarged to  $3.5 \text{ m}^2$ . Pressure loss of adsorption module is 0.3 kPa for the most intensive load.

#### 2.3. Drive module (fan module)

The so called drive module or fan module is another part of the experimental unit. It is responsible for transport of waste gas (flue gas) by using fan (flow rate of  $1000 \text{ m}^3/\text{h}$ , 15 kW engine power supply) which is located in the frame. Frequency converter is to be applied due to need to sustain high pressure losses (to 10 kPa) caused by low flow rate of waste gas.

#### 2.4. Compressor module

This module serves for pulse-jet regeneration of filtration bags utilizing air. It consists of frame and compressor of following characteristics: maximum pressure  $p_{max} = 0.7$  MPa, flow rate of air 2.6 N m<sup>3</sup>/h.

#### 2.5. Module for dosing of adsorbents and liquids

Module doses adsorbents and liquids into inlet pipes in an upstream direction in the experimental unit. This module may also be used for dosing of sodium bicarbonate (NaHCO<sub>3</sub>) in case of dry flue gas cleaning technology test or for dosing of various liquid agents, such as ammonia water in case of NOx disposal tests by using SCR. Membrane pump is used for dosing of liquids; pump dosing ranges from 0 to 2.42 l/h. Powder adsorbent may be dosed at the extent from 0.004 to 0.037 m<sup>3</sup>/h (amount is controlled by frequency converter). Fan is part of the dosing module; it transports adsorbent to higher places while it perfectly disperses it (180 m<sup>3</sup>/h flow rate,  $\Delta p = 2$  kPa).

#### 3. Experiments and results

Tests of catalytic filtration require appropriate operations producing flue gas with usual amount of NOx. MSW incineration plant with maximum processing capacity of 15 t/h was picked out. This incineration plant produces 100,000 m<sup>3</sup>/h of flue gas. Experimental unit is connected to the main flue gas pipe DN 2000 between first and second stage of cleaning, i.e. downstream the ESP and upstream the wet lime cleaning; at this point the concentration of hazardous pollutants reaches values stated in Table 1.

Temperature at the connection ranges from 210 to 240 °C. Part of flue gas is then taken from main flue gas pipe through DN 200 pipe which is equipped with two-phase nozzle dosing 25% ammonia



Fig. 4. 3D model of experimental unit.

water and entry for artificial increase of nitric oxide (NO) concentration by using pressure vessels. Real flow rate of 1000  $m^3/h$  (with -0.6 kPa real pressure and 220 °C temperature) and NOx concentration of 200 mg/N m<sup>3</sup> amount to 0.179 l/h of dosed ammonia water with molar ratio of  $NH_3$ : NO = 1.0 mol/mol. Nitrogen dioxide (NO<sub>2</sub>) makes up less than 2% of overall NOx content, the rest is made up by nitric oxide (NO). Flue gas is then supplied into experimental filtration unit; prior to entering this unit, flue gas may be additionally heated by ca. 20 °C using electro-heating with 5 kW power. Several sampling points are located before entry to the experimental unit. Flue gas then enters the so called distribution chamber and subsequently continues either through by-pass directly to outlet pipe or to filtration section. Clean flue gas enters fan module and passes through orifice where pressure is recorded and real flow rate of flue gas is calculated. Flue gas is then released from the unit through DN 200 pipe back to main flue gas pipe. Several sampling points are again located at the outlet.

PMs are captured on the surface of filtration bags and undergo pulse-jet regeneration; they are subsequently dumped to hopper, packed in bags and stored at hazardous waste landfill. The whole experimental unit including connection is displayed at Fig. 5.

Experimental unit is connected to main flue gas pipe of MSW incineration plant and all functional tests of the unit are performed. REMEDIA<sup>®</sup> filtration material is then tested. This material is used in industrial practice for combined cleaning of flue gas from PMs and disposal of PCDD/F by applying catalytic filtration (Weber et al., 2001). Purposeful addition of ammonia (25% ammonia water) into flue gas stream instigates conditions for side effect of combined flue gas cleaning, i.e. disposal of NOx by using SCR.

lable 1		
Typical concentration of	pollutants at the	point of connection.

Pollutant	Typical concentration $[mg/m_N^3]$ (11% O <sub>2</sub> )	
PM	250	
CO	50	
NOx	200	
HCI	260	
SO <sub>2</sub>	80	

Two analyzators are used to monitor efficiency of filtration material. First device is installed at the inlet and second device at the outlet of the experimental unit. Concentrations of carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), nitric oxide (NO), sulphur dioxide (SO<sub>2</sub>), VOCs and oxygen (O<sub>2</sub>) are continuously measured. Concentration of NOx (expressed as NO<sub>2</sub>) in flue gas entering filtration section of the unit reaches values around 200 mg/N m<sup>3</sup>.

Flue gas entering experimental unit is dosed with 25% ammonia water in various over-stoichiometric ratios (NH<sub>3</sub>:NO = from 1.1 to 2.7 mol/mol). This enables to monitor efficiency of REMEDIA<sup>®</sup> filtration material under standard conditions and also tendency of this material to various nonstandard influences, e.g. with higher over-stoichiometric residue of NH<sub>3</sub>.

In standard conditions, i.e. with over-stoichiometric residue of 1.1 mol/mol, efficiency of new filters in disposal of NOx content is 33.2% (Fig. 6). Efficiency of NOx reduction significantly decreases within a month to ca. 4.5% under nonstandard operational



Fig. 5. Experimental unit.



**Fig. 6.** Standard measured efficiency of new filtration bags in reduction of NOx; average temperature of 228 °C, molar ratio NH<sub>3</sub>:NO = 1.1 mol/mol, average NOx disposal efficiency equaled 33.2%, dry flue gas, concentration recalculated for reference oxygen  $O_2 = 11\%$ .

conditions, i.e. for high over-stoichiometric residues. Gradual decrease of filtration material efficiency for high over-stoichiometric ratios is presented in Fig. 7.

After the experimental tests of filtration material at MSW incineration plant are finished, one of the filtration bags is removed and analyzed in a laboratory (this concerned filtration bag that undergoes test under nonstandard conditions). Efficiency of NOx disposal is measured using two samples from this bag. Standard efficiency of new filtration bag for NOx disposal amounts to 32.5%. Measured efficiency of two samples is 7.7 and 10.8% at the beginning of the laboratory test. Gaseous mixture containing NOx with temperature 230 °C is used as modeling gas. This gas is free of other hazardous compounds. Efficiency increases to 15.0 and 15.8% after 72 h of continuous operation of such laboratory set-up. Following analysis of filtration bag reveals excessive amounts of sulphur compounds, calcium compounds and sodium compounds (Fig. 8). Otherwise, the bag is untouched.

Based on ascertained conditions, following statements may be asserted:



Fig. 7. Comparison of long-term deNOx efficiency for standard and nonstandard conditions.



Fig. 8. Result of filtration bag analysis (diagram presents high amount of sulphur compounds (S), calcium compounds (K) and sodium compounds (Na)).

- Due to low temperature and higher amount of sulphur oxides and ammonia, higher amount of ammonium sulfate/(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>/ is produced, which decreases efficiency of filtration material.
- Sample of filtration material after water extraction; at first it seems untouched (Fig. 9). New tests for deNOx efficiency bring following results 37.9% efficiency, which is even higher than values stated for new filtration material.

Overview of average measured efficiencies during individual phases of the operations and testing of filtration bags is displayed in Fig. 10.

In order to avoid decrease of catalytic layer activity in REMEDIA<sup>®</sup> filtration material during catalytic filtration, it is necessary to prevent creation of sulphur compounds (S), especially ammonium sulfate and other compounds of calcium (K) and sodium (Na). Possibilities of preventing creation of these compounds can be summed up by the following:

- Maintain flue gas temperature between 220 and 240 °C, optimum temperature amounts to 230 °C (Smejkal et al., 2009).
- Decrease amount of NH<sub>3</sub> to technological minimum, i.e. NH<sub>3</sub>:NO = to 1.1 mol/mol; higher molar ratio may result in ammonia slip which may react with substances present in flue gas and subsequently form dangerous compounds (Radivojevic, 1998).
- Prevent contamination of catalytic filtration material with catalytic poisons such heavy metals (As) and alkali metal



**Fig. 9.** Result of analysis of filtration bag after water extraction (diagram reveals no presence of sulphur compounds (S), calcium compounds (K) and sodium compounds (Na)).



Fig. 10. Overview of new filtration bag efficiencies during individual phases of operations and testing.

compounds (Cs<sub>2</sub>O, Rb<sub>2</sub>O, K<sub>2</sub>O, PbO, Na<sub>2</sub>O, Li<sub>2</sub>O, CaO) (Saracco and Specchia, 1998).

- Make sure that ammonia and other compounds used as agent in the process of SCR are well mixed with input flue gas.
- Decrease amount of SO<sub>2</sub> and HCl in supplied flue gas so that there is no formation of dangerous compounds (salts, poisons) (Javed et al., 2007).

If these basic rules are observed, filtration material efficiency should not decrease significantly below the level of new filtration material efficiency.

#### 3.1. Comparison of catalytic filtration with other deNOx methods

Experimental results are compared with average efficiency of other deNOx methods to evaluate the potential for implementation in real operation. The following methods are involved in comparison: SNCR, SCR with fixed-bed catalytic reactor, SCR with catalytic filter and method combining SNCR and SCR with catalytic filter. Comparison of deNOx technologies always has to be based on economic balance and efficiency comparison of individual technologies.

Operational costs of NOx and PCDD/F reduction for catalytic filtration in MSW incineration plant (15 t/h of maximum processing capacity and  $65,000 \text{ N m}^3$ /h of flue gas production) are significantly lower than operation costs for technology based on fixed-bed catalytic reactor (Pařízek et al., 2008; Pavlas and Touš, 2009).



Fig. 11. Example of potential decrease of NOx concentration in flue gas by application of various methods.

However, deNOx efficiency is significantly higher for SCR with fixed-bed catalytic reactor than for SNCR and/or SCR with catalytic filter (90–94% efficiency for SCR with fixed-bed catalytic reactor (European IPPC Bureau, 2008a), 40–70% efficiency for SNCR (European IPPC Bureau, 2008a), 33% efficiency for SCR with catalytic filter (measured)).

Method of SCR with catalytic filter is suitable for high NOx content where SNCR method cannot be applied. Combination of SNCR and SCR with catalytic filter enables sufficient decrease of NOx in flue gas well below emission limits (see Fig. 11) and with lower costs than for installation of SCR based on fixed-bed catalytic reactor only. Fig. 12 presents comparison of investment and operational costs of various deNOx technologies for a MSW incineration plant with flue gas production of 65,000 N m<sup>3</sup>/h. Installation of catalytic filter (baghouse) also solves problem of PMs and PCDD/F emissions since PMs reduction efficiency reaches values of 97% and PCDD/F reduction efficiency amounts to approximately 99% (Dvořák et al., 2009). In general, combination of SNCR and SCR with catalytic filter methods is suitable for 450-650 mg/N m<sup>3</sup> (with 200 mg/N m<sup>3</sup> NOx limit) concentration of NOx in flue gas. If NOx concentration in flue gas is lower than 450 mg/N m<sup>3</sup>, SNCR method may be applied. If the concentration is higher than 650 mg/N m<sup>3</sup>, SCR method with fixed-bed catalytic reactor is more convenient.



**Fig. 12.** Investment and operational costs calculated for three different deNOx technologies for a MSW incineration plant with flue gas production of  $65,000 \text{ N m}^3/\text{h}$  and input NOx concentration of  $550 \text{ mg/N m}^3$  (costs calculations based on European IPPC Bureau, 2008a).

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## A significant contribution to the portfolio of currently used deNOx methods in the form of newly discovered approach based on deNOx/deDiox approach is presented in the paper.

REMEDIA<sup>®</sup> filtration material designed for capture of PMs and PCDD/F is tested for SCR. Tests are performed at newly developed experimental unit which is installed in MSW incineration plant with processing waste capacity of 15 t/h. Average flue gas flow rate amounts to 1000 m<sup>3</sup>/h with 220 °C of temperature. NOx concentration of flue gas usually reaches 200 mg/N m<sup>3</sup>.

Average deNOx efficiency for the tested filtration material reaches 33.2% under standard conditions, i.e. for dosage of 25% ammonia solution in molar ratio of NH<sub>3</sub>:NO = 1.1 mol/mol.

Nonstandard regimes lead to significant SCR efficiency decrease. Filtration bags are examined after nonstandard regime tests and reasons for efficiency decrease are evaluated. Recommendations are then specified to prevent efficiency decrease of this material.

At the end, catalytic filtration is compared with commonly used deNOx methods. It is proven that this method should be combined with SNCR method. This combination should be applied for NOx concentrations ranging from 450 to 650 mg/N m<sup>3</sup> (with 200 mg/N m<sup>3</sup> as NOx limit).

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