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Catalytic Filtration of Flue Gases Polluted by NO_x

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This paper deals with elimination of nitrogen oxides (NO_x) by using the so called catalytic filtration method of selective catalytic reduction (SCR). Series of experimental tests of NO_x reduction was conducted in MSW (municipal solid waste) incineration plant. Various operational conditions were involved and assessment of deNO_x (removal of NO_x) technology was carried out. Two samples of filtration material were later subjected to analysis and evaluated due to decrease of their efficiency during experimental tests under nonstandard conditions (especially for over-stoichiometric ratios NH_3 (ammonia): NO (nitric oxide) higher than 1.1 mol/mol). Catalytic filtration was also compared to other common deNO_x methods. This comparison was based on deNO_x efficiency of particular methods and their investment and operational costs.

1. Introduction

Selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR) are among the basic secondary methods of NO_x reduction in flue gas (Heck et al., 2002; European IPPC Bureau, 2008). SCR may include catalyst in the form of fixed bed, fluid bed and/or the catalyst may be layered on filtration material (fabric or ceramic), i.e. the so called catalytic filtration.

Table 1: Typical concentration of pollutants at the point of connection

Pollutant	*Typical concentration [mg/m_N^3] (11 % O_2)*
PM	250
CO	50
NO_x	200
HCl	260
SO_2	80

Series of tests was carried out in a new experimental filtration unit. The tests analysed efficiency of new catalytic filtration material designed for SCR (i.e. REMEDIA® filtration material provided by W. L. GORE & Associates, Inc.). Experimental unit is designed to process up to 1000 m^3/h of flue gas of 250 °C maximum temperature and may be connected to technology with under-pressure of up to 10 kPa. This unit is installed in MSW incineration plant SAKO Brno, a.s. (Czech Republic) with nominal

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processing capacity of 15 t/h of waste. It was connected to flue gas pipe between electrostatic precipitator (ESP) and wet lime cleaning. At this point, flue gas temperature ranged from 210 to 240 °C and concentration of pollutants reached values stated in Table 1.

2. Experiments and Results

Flue gas entering experimental unit is dosed with 25 % ammonia water in various over-stoichiometric ratios (NH_3: NO = from 1.1 to 2.7 mol/mol). This enables to monitor efficiency of REMEDIA® filtration material under standard conditions and also tendency of this material to various nonstandard influences, e.g. with higher over-stoichiometric residue of NH_3.

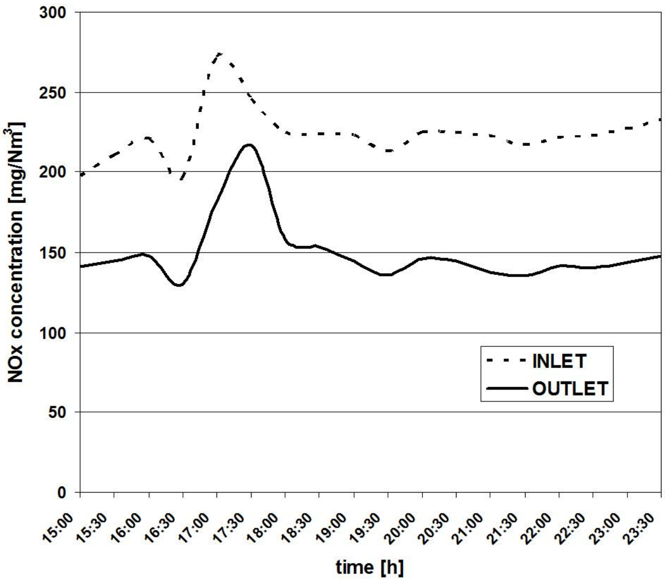

Figure 1: Standard measured efficiency of new filtration bags in reduction of NO_x; average temperature of 228°C, molar ratio NH_3 : NO = 1.1 mol/mol, average NO_x disposal efficiency equaled 33.2 %, dry flue gas, concentration recalculated for reference oxygen O_2 = 11 %

In standard conditions, i.e. with over-stoichiometric residue of 1.1 mol/mol, efficiency of new filters in disposal of NO_x content is 33.2 % (Figure 1). Efficiency of NO_x reduction significantly decreases within a month to ca. 4.5 % under nonstandard operational conditions, i.e. for high over-stoicheiometric residues. Gradual decrease of filtration material efficiency for high over-stoichiometric ratios is presented in Figure 2.

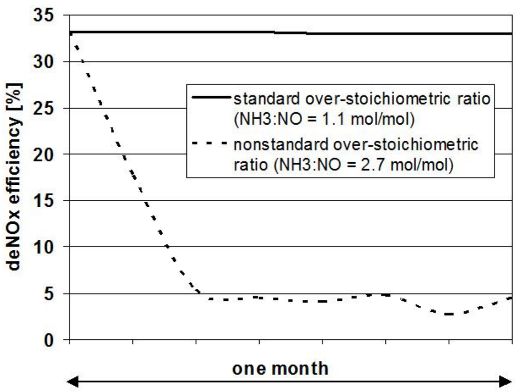

Figure 2: Comparison of long-term deNO$_x$ efficiency for standard and nonstandard conditions

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 NO_x disposal is measured using two samples from this bag. Standard efficiency of new filtration bag for NO_x 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 NO_x 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 hours of continuous operation of such laboratory set-up. Following analysis of filtration bag reveals excessive amounts of sulphur compounds, calcium compounds and sodium compounds. Otherwise, the bag is untouched.
Based on ascertained conditions, following statements may be asserted:

- Due to low temperature and higher amount of sulphur oxides and ammonia, higher amount of ammonium sulfate /$(NH_4)_2SO_4$/ is produced, which decreases efficiency of filtration material.
- Sample of filtration material after water extraction; at first it seems untouched. New tests for deNO$_x$ efficiency bring following results – 37.9 % efficiency, which is even higher than values stated for new filtration material.

In order to avoid decrease of catalytic layer activity in REMEDIA® 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_3 to technological minimum, i.e. NH_3: 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 compounds (Cs_2O, Rb_2O, K_2O, PbO, Na_2O, Li_2O, 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_2 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.

1.1 2.1 Comparison of catalytic filtration with other deNO$_x$ methods

Experimental results are compared with average efficiency of other deNO$_x$ 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 deNO$_x$ technologies always has to be based on economic balance and efficiency comparison of individual technologies.

Operational costs of NO_x and PCDD/F reduction for catalytic filtration in MSW incineration plant (15 t/h of maximum processing capacity and 65,000 Nm^3/h of flue gas production) are significantly lower than operation costs for technology based on fixed-bed catalytic reactor (Pařízek et al., 2008). However, deNO$_x$ efficiency is significantly higher for SCR with fixed-bed catalytic reactor than for SNCR and/or SCR with catalytic filter (90 to 94 % efficiency for SCR with fixed-bed catalytic reactor (European IPPC Bureau, 2008), 40 to 70 % efficiency for SNCR (European IPPC Bureau, 2008), 33 % efficiency for SCR with catalytic filter (measured)).

Method of SCR with catalytic filter is suitable for high NO_x content where SNCR method cannot be applied. Combination of SNCR and SCR with catalytic filter enables sufficient decrease of NO_x in flue gas well below emission limits (see Figure 3) and with lower costs than for installation of SCR based on fixed-bed catalytic reactor only. Figure 4 presents comparison of investment and operational costs of various deNO$_x$ technologies for a MSW incineration plant with flue gas production of 65,000 Nm^3/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 % (Pařízek et al., 2008). In general, combination of SNCR and SCR with catalytic filter methods is suitable for 450 to 650 mg/Nm^3 (with 200 mg/Nm^3 NO_x limit) concentration of NO_x in flue gas. If NO_x concentration in flue gas is lower than 450 mg/Nm^3, SNCR method may be applied. If the concentration is higher than 650 mg/Nm^3, SCR method with fixed-bed catalytic reactor is more convenient.

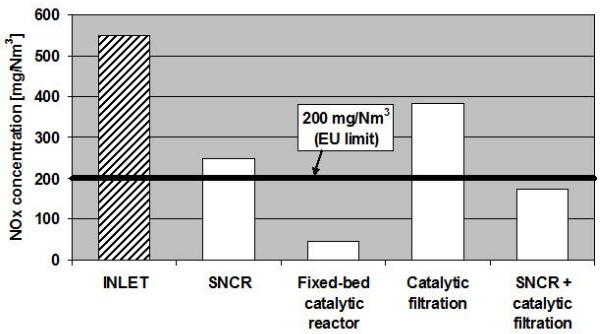

Figure 3: Example of potential decrease of NO_x concentration in flue gas by application of various methods

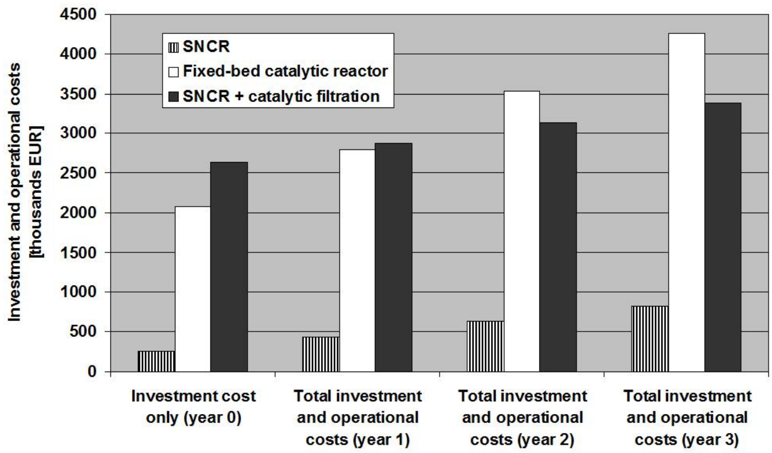

Figure 4: Investment and operational costs calculated for three different deNO_x technologies for a MSW incineration plant with flue gas production of 65,000 Nm^3/h and input NO_x concentration of 550 mg/Nm^3 (costs calculations based on European IPPC Bureau (2008))

3. Conclusion

REMEDIA® filtration material designed for capture of PMs and PCDD/F is tested for selective catalytic reduction of NO_x (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^3/h with 220 °C of temperature. NO_x concentration of flue gas usually reaches 200 mg/Nm^3.

Average deNO_x 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_3 : 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 NO_x concentrations ranging from 450 to 650 mg/Nm^3 (with 200 mg/Nm^3 as NO_x limit).

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