Simultaneous NO\textsubscript{x} and SO\textsubscript{2} removal in wet and semi-dry FGD

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Abstract

Since 80. of the last century many investigations have been made on the application of NO oxidation to higher oxides in order to remove them from flue gas in water solution of NaOH or in suspensions of CaCO\textsubscript{3} and Ca(OH)\textsubscript{2}. This method of flue gas de-nitrification hasn’t got industrial applications yet because the development of low-NO\textsubscript{x} burners made possible to reduce the NO\textsubscript{x} content in exhaust gases approximately from 1000 to 400 mg/m\textsuperscript{3}, which satisfies the EU emission limits up to 2016. Actually, the technology of NO oxidation again is getting serious concern because the NO removal efficiency obtained with two-step process is better than 90% without an expensive installation of SCR. The investment is similar like SNCR, however without its negative effects (NH\textsubscript{3} in flue gas and ash). The studies conducted at the Wrocław University of Technology are the first approach to develop new, wasteless technology of NO\textsubscript{x} removal based on O\textsubscript{3} or H\textsubscript{2}O\textsubscript{2} injection into exhaust gases before a scrubber of existing wet flue gas desulphurisation installations. The results of this preliminary, laboratory studies, in which flue gas (0.2 m\textsuperscript{3}/h) from the pulverized hard coal-firing boiler (OP-430) was used, have showed the efficiency of reduction of NO\textsubscript{x} emission in the range of 84-85% at the temperature 60-80 °C.

1. Introduction

Demand to reduce the NO\textsubscript{x} (NO+NO\textsubscript{2}) emission (below 200 mg/m\textsuperscript{3} in the EU countries after 2016) from large combustion plants have resulted development of methods of NO removal based on reduction of NO by ammonia. The related technologies (SCR and SNCR) are expensive because they require ammonia synthesized mainly of methane (in fact of natural gas). An alternative approach is based on the oxidation of NO to NO\textsubscript{2}, N\textsubscript{2}O\textsubscript{4}, N\textsubscript{2}O\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} (further denoted NO\textsubscript{y}) in semi-dry and wet flue gas desulphurisation (FGD) installations. The products of NO\textsubscript{y} sorption, mainly (Ca(NO\textsubscript{3})\textsubscript{2}), would be removed together with CaCl\textsubscript{2}, in the wet FGD sewage or with the products of semi-dry absorption (SDA) method (CaSO\textsubscript{3}, CaSO\textsubscript{4}, CaCl\textsubscript{2}, Ca(NO\textsubscript{3})\textsubscript{2}, Ca(OH)\textsubscript{2}). Reduction of Hg\textsuperscript{0} emission using this technology wouldn’t require additional costs. When the proposed method would be combined with SDA the
presence of Ca(NO₃)₂ in waste product is meaningless because in products of SDA there are CaSO₃ and CaCl₂, which have to be storage safely. If NO is oxidized to NOₓ before wet FGD, the increase of salt Ca(NO₃)₂ in the suspension being sprayed in the scrubber and, next, in the sewage after washing of CaSO₄·2H₂O, won’t be a great problem, nevertheless it should be considered. After re-crystallisation and separation of CaCl₂ and the rest of CaSO₄·2H₂O from sewage the remaining solution of approx. 50% of Ca(NO₃)₂ could be used as an mineral fertilizer.

These investigations are continuation of a cycle of technological studies of the processes of flue gas conditioning by injection of sorbents [2, 3]. The developed technologies of simultaneous removal of SO₂ and NOₓ [4, 5, 6, 7] satisfy technical and economic requirements, and allow to apply them for cleaning of flue gas from coal-fired utility boilers of small and medium units (20-200 MWₑ). The application of these technologies to cleaning of exhaust gases from waste thermal incinerators is particularly recommended. Removal of products of NO oxidation together with HCl and SO₂ in wet or dry-scrubbing apparatus permits to diminish NOₓ content in flue gas below 50 mg/m³ at much lower costs than combining SCR and FGD installations.

2. Review of NO, NO₂, N₂O₅, N₂O₄, N₂O₃, N₂O properties

The major source of nitrogen oxides are processes of fuel burning in which two mechanisms of NOₓ formation are the most significant. The first mechanism is synthesis of NO: N₂ + O₂ = 2NO being important at the temperature above 1600 K. The second mechanism includes complex conversion of nitrogen compounds in fuel into NO in combustion process. This mechanism is responsible for the main part of NOₓ emission during burning of solid fuels and heavy oil. In atmosphere NO is oxidized to NO₂ being a source of higher oxides (N₂O₃, N₂O₄ and N₂O₅), which are toxic and take part in many reactions in gaseous and liquid phase (unlike NO, NO₂, N₂O₃, N₂O₄ and N₂O₅ are highly soluble in water and form acids HNO₂ and HNO₃). Selected properties of nitrogen oxides and ozone were shown in Table 1.
Table 1. Properties of nitrogen oxides and ozone

<table>
<thead>
<tr>
<th>Property</th>
<th>NO</th>
<th>N₂O</th>
<th>NO₂</th>
<th>N₂O₃</th>
<th>N₂O₄</th>
<th>N₂O₅</th>
<th>Ozone O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic mass, g/mol</td>
<td>30.006</td>
<td>44.013</td>
<td>46.005</td>
<td>76.01</td>
<td>92.011</td>
<td>108.01</td>
<td>47.998</td>
</tr>
<tr>
<td>Density (at 298 K) kg/m³</td>
<td>Liquid</td>
<td>1.3</td>
<td>1.2228</td>
<td>1.443</td>
<td>1.4</td>
<td>1.443</td>
<td>2.144</td>
</tr>
<tr>
<td></td>
<td>Vapor</td>
<td>1.34</td>
<td>1.8</td>
<td>3.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melting temperature, °C</td>
<td>-163.6</td>
<td>-90.86</td>
<td>-11.2</td>
<td>-0.1</td>
<td>-11.2</td>
<td>41</td>
<td>-197.2</td>
</tr>
<tr>
<td>Boiling temperature, °C</td>
<td>-151.7</td>
<td>-88.48</td>
<td>21.1</td>
<td>3.0</td>
<td>21.1°C</td>
<td>decompose</td>
<td>-111.9</td>
</tr>
<tr>
<td>Enthalpy, kJ/mol</td>
<td>+82.05</td>
<td>-35.05</td>
<td>+142.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Color</td>
<td>colorless</td>
<td>colorless</td>
<td>tawn</td>
<td>celeste liquid</td>
<td>transparent</td>
<td>white powder</td>
<td>celeste gas</td>
</tr>
<tr>
<td>Solubility in water, g/dm³</td>
<td>0.032</td>
<td>0.111</td>
<td>213.0</td>
<td>500.0</td>
<td>213.0</td>
<td>500.0</td>
<td>1.05</td>
</tr>
</tbody>
</table>

1 solubility of SO₂: 27 g/dm³ at 50 °C and 5.8 g/dm³ at 90°C

The analysis of the times of NO to NO₂ oxidation in air (Table 2) showed that the idea of NO oxidation in flue gas before a scrubber of FGD is promising. Well known in the atmospheric chemistry facility of NO oxidation in air assures that this process will be more effective when active oxidants (O₃, H₂O₂, NaOCl, Ca(ClO)₂) are used. It is beyond doubts that the products of NO oxidation will be absorbed in wet and semi-dry absorbers of FGD, where the temperature in scrubbers is the range of 50-70 °C (solubility of nitrogen oxides and SO₂ was compared in Table 1). These properties of nitrogen oxides became the basis of the development of new technologies of flue gas cleaning called “Multi-Pollution Control”.

The first considered method (USA patent [1]) relies on NO oxidation by ozone in preliminary cooled flue gas to the temperature 60-70 °C by injection of water (0.67-10.7 m³ H₂O/1000 m³ flue gas). In the next step the products of NO oxidation were removed from flue gas in the column by water flowing down the walls. The ratio O₃/NO was in the range of 0.5–3.5 mol/mol and the residence time t_res was 0.5–1.0 s. It appeared to be possible to reduce NO content below 50 mg/m³ and the obtained efficiency of flue gas cleaning was better than 90%.

The liquid injected into flue gas had pH in the range of 5.5-7.5 and could contain compounds of sodium, calcium and magnesium. It results from description of the process that for O₃/NO = 1.2 – 2.2 it is be possible to remove above 90% of NO from flue gas when ozone content in air blown into the column is 3.5%. Longer residence time demanded less ozone necessary for NO oxidation.

Table 2. Time of NO oxidation to NO₂ in air (50%) depending on NO content

<table>
<thead>
<tr>
<th>NO content ppm</th>
<th>Oxidation time mg/m³ mins</th>
<th>NO₂ content ppm</th>
<th>Rest of NO mg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 000</td>
<td>26 786</td>
<td>10 000</td>
<td>13 393</td>
</tr>
<tr>
<td>10 000</td>
<td>13 393</td>
<td>5 000</td>
<td>6 696.5</td>
</tr>
<tr>
<td>1000</td>
<td>1339.3</td>
<td>500</td>
<td>669.65</td>
</tr>
<tr>
<td>300</td>
<td>401.8</td>
<td>150</td>
<td>200.9</td>
</tr>
<tr>
<td>100</td>
<td>134.0</td>
<td>50</td>
<td>67.0</td>
</tr>
<tr>
<td>10</td>
<td>13.4</td>
<td>5</td>
<td>6.7</td>
</tr>
<tr>
<td>1</td>
<td>1.34</td>
<td>0.5</td>
<td>0.67</td>
</tr>
</tbody>
</table>
The second technology of reduction of NO\(_x\) emission relies on injection of dispersed water with H\(_2\)O\(_2\) into flue gas flowing through the reactor [8]. The oxidant and NO were activated by electromagnetic (microwave) radiation, having one of the frequency: 915, 2450, 5800, and 22 125 MHz, which helps to generate reactive radicals OH and HO\(_2\). Microwave radiation quickly rises the temperature of H\(_2\)O\(_2\) droplets, e.g. from the room temperature to 152 °C (temperature of H\(_2\)O\(_2\) boiling) in 0.05-3.3 s. The molar ratio of the oxidant and NO should be approximately stoichiometric (H\(_2\)O\(_2\):NO = 1:1 mol/mol). The oxidation reaction is then very effective: 80-90% of NO was oxidized to higher oxides. When adding methanol to the solution of H\(_2\)O\(_2\) in water, SO\(_3\) was reduced to SO\(_2\) and CO oxidized to CO\(_2\). From the description of the laboratory experiment it results that the NO content in carrier gas decreased from the initial 1200 to 4-10 ppm, finally [8].

The third method, called ECO (Electro-Catalytic Oxidation [9]), relies on a three steps procedure of flue gas cleaning:
- in the first step more than 90% of dust is removed from exhaust flue gas in the electrostatic precipitator,
- in the second step high energy electrons are generated, which attack molecules to produce radicals:
  \[ \text{O}_2 + e \rightarrow \text{O} + \text{O} + e \]
  \[ \text{H}_2\text{O} + e \rightarrow \text{OH} + \text{O} + e \]
  \[ \text{O} + \text{H}_2\text{O} \rightarrow 2\text{OH} \]
  which react with NO, SO\(_2\) and Hg\(^0\) at the low temperature range of 65-150 °C,
- in the third step NO\(_2\), HNO\(_3\), H\(_2\)SO\(_4\), HgO are removed from the exhaust gas.

The mentioned and other publications confirmed the ability of the considered methods to simultaneous removal of NO\(_x\), SO\(_2\) and Hg from exhaust gases, however, they haven’t been converted into commercial technologies yet. The main objective of the investigations reported was to examine one of basic element of these technology i.e. oxidation of NO by ozone in flue gas from a hard coal-fired boiler.
3. Experimental

A schematic diagram of the experimental apparatus was shown in Fig. 1. Flue gas was taken from the by-pass 1 of flue gas duct in the OP 430 boiler by the fan 2 to the WAWO-2 installation. From the collector 3 flue gas (200 dm$^3$/h) was flowing into the spiral reactor, in which was mixed with air containing 6% of ozone produced by the ozonizer 5. The spiral (ozonizing) reactor 4 was made of a spirally curled polypropylene pipe of 10 mm in the diameter and of 1.6 m in the length. The major part of air/ozone stream was evacuated into the flue gas duct, only 0.7-2.1 m$^3$/h was directed by the pump 6 to the ozonizing reactor 4 for NO oxidation. The combined streams of flue gas and air/ozone (approx. 200 dm$^3$/h) were flowing with the velocity 0.35-1.07 m/s through the ozonizing reactor 4 and mixing together (at the temperature 60-90 °C) for the residence time $t_{res} = 3.3-10.7$. Products of the reactions were removed from flue gas in the absorber 7 by sorbent (5% of NaOH in water). Cleaned flue gas were directed by the pump 10 through the dryer 8, the flow-meter 9 and the gas-meter 11 to the by-pass duct 1. The content of NO and O$_2$ in flue gas before the ozonizing reactor 4 and after the gas-meter 11 was measured using two gas analyzers Madur GA-40 (A1 and A2).

![Schematic diagram of the experimental apparatus](image)

**Fig. 1. Schematic diagram of the experimental apparatus:** 1 – by-pass of flue gas, 2 – fan, 3 - flue gas collector, 4 – reactor, 5 – ozonizer, 6 – doze pump, 7 – absorber, 8 – dryer, 9 – flow-meter, 10 – pump, 11 – gas-meter, 12 – OP 430 boiler, 13 – heat exchanger, 14 – electrostatic precipitator, 15 – flue gas fan, 16 – flue gas duct, 17 – chimney, 18 – pilot installation WAWO-2, A1 and A2 – gas analyser
When ozone was injected into the spiral reactor 4, NO was oxidized by the following reactions:

\[ \text{NO} + \text{O}_3 = \text{NO}_2 + \text{O}_2 \]
\[ 2 \text{NO} + \text{O}_3 = \text{N}_2\text{O}_3 + \text{O}_2 \]
\[ 2 \text{NO} + 2\text{O}_3 = \text{N}_2\text{O}_5 + 3/2 \text{O}_2 \]

The higher oxides of nitrogen are soluble in water and the following reactions took place in the absorber 7 (2 or 3 washers):

\[ \text{NaOH} + \text{HNO}_2 = \text{NaNO}_2 + \text{H}_2\text{O} \]
\[ \text{NaOH} + \text{HNO}_3 = \text{NaNO}_3 + \text{H}_2\text{O} \]
\[ 2\text{NaOH} + \text{SO}_2 = \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \]

The excess of ozone in air was converted into O₂ by the reactions:

\[ \text{NaNO}_2 + \text{O}_3 = \text{NaNO}_3 + \text{O}_2 \]
\[ \text{Na}_2\text{SO}_3 + \text{O}_3 = \text{Na}_2\text{SO}_4 + \text{O}_2 \]

The effectiveness of NO removal from flue gas in the experiment was defined as follow:

\[ \eta = 1 - \frac{[\text{NO}]}{[\text{NO}]} \]

where subscripts 1 and 2 correspond to the measured [NO] by the gas analysers A1 and A2.

4. Results

4.1 Influence of the temperature

It was found that the temperature only slightly influences the effectiveness of NO removal \( \eta \) from flue gas (Fig. 2), e.g. for the molar ratio \([\text{O}_3/\text{NO}] = 0.9 \text{ mol/mol}\):

- \( \eta = 84\% \) at 60 °C,
- \( \eta = 86\% \) at 90 °C.

![Fig. 2. The effectiveness of NO removal (\( t_{\text{res}} = 5 \text{ s}, [\text{O}_3/\text{NO}] = 0.9 \text{ mol/mol} \)) vs. temperature](image-url)
Analyzing the influence of the temperature, one should take into consideration that the rate of NO oxidation by ozone in gas phase (NO + O₃ = NO₂ + O₂) slightly accelerates when the temperature increases. The second important process is formation of HNO₂ and HNO₃ in reaction NO₂ with steam; durability of HNO₂ molecule decreases when the temperature rises. During this experiment the second effect was not important because of low temperature at the absorber 7 (25-35 °C).

**4.2 Influence of ozone excess**

The main purpose of this part of study was to show high effectiveness of NO removal from flue gas under substoichiometric molar ratio; [O₃/NO] < 1. The effect of ozone excess on the efficiency of NO removal was examined in the range of [O₃/NO] = 0.87-1.48 mol/mol and at the temperature in the ozonizing reactor \( T_r = 60 \) °C. The flow rate of flue gas was approximately 200 dm³/h. Fig. 3 shows that the increase of the ratio [O₃/NO] to 1.5 only slightly improve the effectiveness of NO removal; approximately to 91%.

![Fig. 3](image-url)
4.3 Influence of residence time $t_{\text{res}}$

The effect of residence time in the ozonizing reactor $t_{\text{res}}$, which was varying in the range of 3.4-10.0 s, was investigated for the ozone excess $[O_3/NO] = 1.3-1.36$ mol/mol and at the temperature $T_i = 60 \, ^\circ\text{C}$ (Fig. 4). The increase of residence time from 4 to 10 s improved the effectiveness of NO removal only about 10%.

![Effectiveness vs. Residence Time](image)

Fig. 4. The effectiveness of NO removal vs. residence time $t_{\text{res}}$ ($[O_3/NO] \approx 1.3, T_i = 60 \, ^\circ\text{C}$)

5. Economy of NO$_x$ removal

The cost of exhaust gas de-nitrification was analyzed for the following parameters of the process of NO removal:

- $t_{\text{res}} = 5$ s,
- $T_i = 90 \, ^\circ\text{C}$,
- $[O_3/NO] = 1.3$ mol/mol,
- required ozone to remove NO: $[O_3/NO_2] = 1.492$ kg/kg
- $\eta = 90\%$.

The balance was made for the boiler OP 650 characterized by the following parameters:

- flow rate of flue gas: 800 000 m$^3$/h,
- temperature of flue gas before the wet FGD: 373 K,
- SO$_2$ concentration before and after the absorber: 2.0 g/m$^3$ and 0.4 g/m$^3$, respectively,
- NO concentration before ozone injection: 196 mg NO/m$^3$,
- NO$_2$ concentration after the reactor: 200 mg NO$_2$/ m$^3$ (130 mg NO/m$^3$),
- flow rate of NO(NO₂): 54 NO kg/h (82.8 NO₂ kg/h)
- the residence time of flue gas and ozone: 5 s,
- flow rate of ozone: 112.3 kg/h,
- flow rate of HNO₃ produced due to NO oxidation: 113.4 kg/h,
- flow rate of CaCO₃ to neutralization of HNO₃: 90 kg/h,
- flow rate of Ca(NO₃)₂: 147.6 kg/h,
- flow rate of CaSO₄: 2720 kg/h (3440 CaSO₄•2H₂O kg/h),
- flow rate of sewage from wet FGD: 6 m³/h,
- concentration of Ca(NO₃)₂ in sewage: 24.6 kg/m³ (2.46%),
- need of electric energy for ozone generation: 16 kWh/kg O₃,
- inner costs and market price of electric energy: 90 and 122 PLN/MWh.

According to the above assumptions the cost of removal of 1 kg of NO₂ from flue gas was calculated (for the inner cost of electric energy) as follow:

\[
90 \text{ PLN/MWh} \times 0.016 \text{ MWh/kg O}_3 \times 1.492 \text{ kg O}_3 = 2.15 \text{ PLN}
\]

The comparison of the costs of NO removal from flue gas in the OP 650 boiler was presented in Table 3.

### Table 3. Comparison of NO removal from flue gas depending on the method used

<table>
<thead>
<tr>
<th>Technology</th>
<th>Cost/price of electric energy/ammonia,</th>
<th>Cost of NO removal, PLN/kg NO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO oxidation</td>
<td>Cost of electric energy: 90 PLN/MWh</td>
<td>2.15</td>
</tr>
<tr>
<td>SCR</td>
<td>Price of electric energy: 122 PLN/MWh</td>
<td>2.92</td>
</tr>
<tr>
<td>SCR</td>
<td>Price of ammonia: 400 USD/Mg</td>
<td>4.04</td>
</tr>
</tbody>
</table>

These data should be completed by the fact that the price of ammonia is increasing following the rising price of natural gas. The second important information is that the calculated investment costs, depending on the installed electric power, were estimated: 5 USD/kWₑ and 150 USD/kWₑ for described method of NO removal and SCR, respectively.

### 6. Summary

These investigations confirmed that the two-step procedure of NOₓ removal applying the oxidation of NO by ozone and removal of the products of NO oxidation in FGD is effective and economic. The obtained results have made possible to determine the technical and economic parameters of the process.

Actually, a common approach to satisfy the limit of NOₓ emission 200 mg/m³ in the EU countries is reduction of NO by ammonia in SCR. In Polish power plants SCR hasn’t been installed yet, however they are equipped with wet FGD, which makes possible to apply the proposed two-step procedure of NO removal. De-nitrification of flue gas is then simple
because requires only deliver of ozone to the duct of flue gas before wet FGD. It is also much cheaper than SCR.

The same method of NO removal could also be combined with the semi-dry flue gas desulfurization, which are actually used in many small and medium coal-fired boilers in Poland. It could be even easier than combining with wet FGD, because wastes from semi-dry FGD (CaSO₃, CaSO₄, CaCO₃, CaCl₂ and Ca(OH)₂) cannot be utilized and have to be safely stored, which could be done together with Ca(NO₃)₂ and mercury salts.
REFERENCES


