Efficient use of Steam Injection for Suppression of NOX Emission in Gas-Turbines Engines

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Abstract: The article is devoted to the water steam injection use efficiency for the purpose of NOx emissions suppression in gas-turbine units. There was described the problem of saving the maximum allowable concentration of nitrogen oxides in the near-ground layer the alternative decision for what was the reduction of nitrogen monoxide concentration. As the result of tests there was confirmed the high efficiency of suppression of NOx emission by steam. On the basis of the received results there was made a conclusion concerning the occurrence of necessary preconditions for the review of the role of steam in the technology of NOx emission wet suppression.

Keywords: Water steam injection, NOx, emission suppression, gas-turbine units, reduction of nitrogen monoxide concentration.

1. Introduction

The realia of modern world power-generating necessitate the introduction of gas-turbine and vapor-gas units (GT unit and CCGT unit) that is one of the perspective trends of the further improvement of fuel-and-power sector. On the current stage, the power-generating GT unit and CCGT unit work mainly on natural gases, not containing sulphurs and other harmful admixtures. It has been established that when functioning at the GT unit full load the exhaust gases from such fuel combustion don’t contain other emissions except the toxic nitrogen oxides forming in the combustion chamber. The table 1 shows the maximum allowable concentration (mac) specified by sanitary-hygienic norms of their concentration values in the air of populated locations that characterize their toxicity degrees.

Table 1. The maximum allowable concentration (mac) in the air of populated locations that characterize their toxicity degrees (mg/m³)

<table>
<thead>
<tr>
<th>Emission</th>
<th>Max one-time dose</th>
<th>Average daily dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>0,060</td>
<td>0.06</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.085</td>
<td>0.04</td>
</tr>
</tbody>
</table>

The most toxic of all the nitrogen oxides is nitrogen dioxide. Analyzing the global contamination of atmosphere it’s usually taken into account the sum of nitrogen oxides as in natural conditions NO oxidizes to NO₂ and NO is converted to NO₂

\[ NO + NO₂ = NOX \]

Thus the actual toxicity of the gases [6] is estimated by the formula

\[ F_{NOx} = \frac{C_{NOx}}{mac_{NOx}} \]

\[ NOx = \frac{C_{NOx}}{0.085} \]

where the NOx concentration in GT unit exhaust gases is usually reduced to 15% O₂.

The real composition of nitrogen oxides, entering the near-ground layer of the atmosphere (at the human respiration level), and their actual toxicity can differ since they depend upon processes, accompanying the diffusion of the exhaust gases tail in the atmosphere, and internal chamber processes, as well as upon the method of suppression of NOx emission, implemented in GT unit. There is a possibility of the formation of a certain amount of NOx in the pre-flame zone of the combustion chamber [5, 11], but it’s usually inconsiderable, especially taking into account the fact that its bigger part decomposes in flame [5]:

\[ NO₂ + O → NO + O₂ \]

Due to this the composition of nitrogen oxides, exiting the combustion chamber and GT unit, is defined basically by the process of post-flame thermal oxidation of the air nitrogen.

The model of this process was described by Zel’dovich [1]

Table 2: The values of nitrogen emissions with the combustion products for gas-turbine units [4]

<table>
<thead>
<tr>
<th>GT unit type</th>
<th>Combustion products discharge, m³/s</th>
<th>Intensity of emission, NOx g/s</th>
<th>NOx concentration mg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>GT-700-5</td>
<td>35,4</td>
<td>6,89</td>
<td>200</td>
</tr>
<tr>
<td>GTK-5</td>
<td>35,4</td>
<td>6,89</td>
<td>200</td>
</tr>
<tr>
<td>GT-6-750</td>
<td>37,1</td>
<td>3,57</td>
<td>100</td>
</tr>
<tr>
<td>GTN-6</td>
<td>37,1</td>
<td>3,57</td>
<td>100</td>
</tr>
<tr>
<td>GT-750-6</td>
<td>45,6</td>
<td>15,5</td>
<td>350</td>
</tr>
<tr>
<td>GPA-II-6,3</td>
<td>47,1</td>
<td>3,04</td>
<td>70</td>
</tr>
<tr>
<td>GPU-6</td>
<td>23,3</td>
<td>2,41</td>
<td>109</td>
</tr>
<tr>
<td>GPA-II-8</td>
<td>47,8</td>
<td>4,83</td>
<td>110</td>
</tr>
<tr>
<td>GPU-10</td>
<td>68,1</td>
<td>4,3</td>
<td>70</td>
</tr>
<tr>
<td>GTN-10I</td>
<td>40,6</td>
<td>7,68</td>
<td>20</td>
</tr>
<tr>
<td>GTN-8</td>
<td>66,6</td>
<td>11,7</td>
<td>180</td>
</tr>
<tr>
<td>GTK-16</td>
<td>79,2</td>
<td>7,57</td>
<td>100</td>
</tr>
<tr>
<td>GTN-16</td>
<td>67,4</td>
<td>11,6</td>
<td>180</td>
</tr>
<tr>
<td>GTN-16M-1</td>
<td>66,6</td>
<td>8,88</td>
<td>108</td>
</tr>
<tr>
<td>GPA-II-16</td>
<td>80,5</td>
<td>7,73</td>
<td>100</td>
</tr>
<tr>
<td>GPU-16</td>
<td>76,2</td>
<td>6,4</td>
<td>88</td>
</tr>
<tr>
<td>GTN-25</td>
<td>117,3</td>
<td>13,4</td>
<td>120</td>
</tr>
</tbody>
</table>
Several reactions are known to generate HO\textsubscript{2} radical [2]. The main of them occur at comparatively low temperatures (less than 800-900 K [6]) and are realized according to the triple concussion scheme:

\[ H + O_2 + M \rightarrow HO_2 + M \]

where M is any third molecule, the purpose of which is to energetically stabilize the radical [2].

As far as the temperatures, under which the oxidation of CH\textsubscript{4} takes place, are concerned, there is also certain probability of the following reaction:

\[ CHO + O_2 \rightarrow CO + HO_2 \]

According to the above-mentioned particularities of this process at full load modes of GT unit, the concentration of HO\textsubscript{2} in the combustion chamber and, consequently, the concentration of NO\textsubscript{2} on the output from it is usually small; the exhaust gases contain mainly NO. However, upon its exiting from the exhaust pipe, NO gradually oxidizes to NO\textsubscript{2}, influence by atmospheric ozone:

\[ NO + O_2 \rightarrow NO_2 + O \]

Considering the expression NO\textsubscript{2}/N0\textsubscript{X}, it can be noticed that in connection with the peculiarities of this process this ratio increases.

Consequently the total actual toxicity rate of nitrogen oxides emissions in the exhaust gases tail also begins to increase:

\[ F_X = F_{NO} + F_{NO2} \]
\[ F_X = C_{NO}/0.6 + C_{NO2}/0.085 \]

To preserve the threshold concentration rate of nitrogen oxides in the near-surface level under such conditions is possible only by increasing the exhaust gases diffusion in the atmosphere by the means of increase the height of the smokestacks N, the cost of which in single-pipe variant is equal to [8]

\[ K \approx H^{2.2} \]

Summing up the above-stated it’s obvious that the underperforming measures require an alternative decision like the reduction of nitrogen monoxide output concentration. In accordance with mechanism of nitrogen monoxide formation [1], this can be furthered by reduction of the maximum temperature in the reaction area of the combustion chamber and the time of reagent presence within the zone of these temperatures. At present, most methods of the reduction of nitrogen oxides emissions are realized by temperature values reduction [3, 7].

The authors have researched the impact of water steam (H\textsubscript{2}O) injection into the combustion chamber on nitrogen oxides emission and composition.

This method differs by its constructive simplicity and is considered to be very efficient, in spite of its negative consequences. Consequently this method is used in GT unit and CCGT unit both as the target, so-called “ecological” steam injection, and as a component of the “energy-generating” injection (which serves the purpose of increasing of capacity and efficiency of CCGT unit - monarCCGT units of STIG type); as well as a reserve method for NO\textsubscript{X} suppression, auxiliary to the main one.

Remember about the air temperature supplied into the combustion area as there is the dependence between the number of nitrogen oxide emissions and the air temperature in chamber (figure 1).

The results of the test of model combustion chamber at vapor injection into the flow of initial air are shown in Figure 2 in the form of the following relations

\[ NO_X = f(G_{H2O}/G_{fuel}) \]

Where \( G \) – mass consumption;
\( T_3 \) – temperature of the gases at output from the combustion chamber. \( T_3 \approx 1150K \)

\[ K \approx H^{2.2} \]

\[ N_O \text{ from the air preheating temperature before the combustion chamber, } \% \]

\[ 100 \]
\[ 75 \]
\[ 50 \]
\[ 25 \]
\[ 0 \]
\[ 150 \]
\[ 200 \]
\[ 250 \]
\[ 300 \]
\[ 350 \]

\[ Air \text{ preheating temperature, } ^{\circ}C \]

\[ NO_{X}, NO_{Y} \text{ mg/m}^3 \]

\[ 0 \]
\[ 0.04 \]
\[ 0.08 \]
\[ 0.12 \]
\[ 0.16 \]
\[ 0.2 \]
\[ 0.24 \]

\[ T = 1273 K \]

\[ T = 1473 K \]

\[ NO, NO_2 \text{ mg/m}^3 \]

\[ 0 \]
\[ 10 \]
\[ 20 \]
\[ 30 \]
\[ 40 \]

\[ CO/Fuel \text{ mol/mol} \]

\[ 0.05 \]
\[ 0.1 \]
\[ 0.15 \]
\[ 0.2 \]

\[ NO_x, NO_y \text{ mg/m}^3 \]

\[ 0 \]
\[ 0.04 \]
\[ 0.08 \]
\[ 0.12 \]
\[ 0.16 \]
\[ 0.2 \]
\[ 0.24 \]

\[ NO, NO_2 \text{ mg/m}^3 \]

\[ 0 \]
\[ 10 \]
\[ 20 \]
\[ 30 \]
\[ 40 \]

\[ CO/Fuel \text{ mol/mol} \]

\[ 0.05 \]
\[ 0.1 \]
\[ 0.15 \]
\[ 0.2 \]
a) the influence of relative emission supplied into the steam combustion chamber $G_{rel}/G_{fuel}$ on the NO$_X$ components at $T_{cp}=1473$ K;

b) the dependence between the relative content of NO$_2$/NO$_X$ from $G_{rel}/G_{fuel}$ and $T_{cp}$.

To receive the actual results there was made an imitative model of nominal state of GT unit operation with maximum NO$_X$ concentration in a one-shaft GT unit design and with maximum NO$_X$ concentration and maximum mass gases emissions due to the maximum speed of turbine compressor (gas generator) in a two-shaft GT unit design. The results confirm the high efficiency of the suppression of NO$_X$ emissions by the means of steam. E.g., at steam consumption rate 0.5, the consumption of NO$_X$ fuel decreases from 98 to 55 mg/m$^3$ i.e. in 1.8 time, whereas at steam consumption rate equal to fuel consumption it decreases in 3 times.

The figure 2 (a) illustrates the same results displaying the NO$_X$ decomposition into its components: NO and NO$_2$. It’s obvious from the comparison between the curves the defining role of NO in NO$_X$ concentration decrease at steam injection into the combustion chamber.

The concentration of NO$_2$ at steam injection, in spite of drastic reduction of NO concentrations, doesn’t decrease but even somewhat increases. As a result, the steam injection into the combustion chamber is accompanied by a drastic increase of NO$_2$ i.e. NO$_2$/NO$_X$ relative content in the exhaust gases (figure 2, b).

This is possible only if the concentration of HO$_2$ radical at steam injection increases in the chamber. For it to be formed, along with the triple concusion also atomic hydrogen is needed. It is believed [6] that at combustion in normal atmosphere (without steam) the main source of the atomic hydrogen, required for this reaction, is carbon oxides burning-out reaction taking place at 900-1100 K:

$$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$$

Probably, at steam (H$_2$O) injection into the combustion chamber to the atomic hydrogen, generated by the reaction, is added also the atomic hydrogen, forming at the process of thermal dissociation of the water steam injected into the camera, which begins at 875 K and rapidly progresses at further increase of the vapor heating temperature.

From the above-stated we can conclude that steam injection into the combustion chamber influences upon nitrogen oxides emission not only by reduction of thermal level in the reaction area, but also by a direct impact on chemical processes, which results in a drastic increase of NO$_2$/NO$_X$ correlation in the exhaust gases. This results, in its turn, in a similarly drastic change of the output (at exiting from smokestack) level of actual toxicity of emitted gases $F_N$ in comparison with its estimation based on NO$_X$ content, as well as a weak dependency of this toxicity upon steam concentration (Figure 3).

At parameters, typical for GT unit exhaust gases (R = 0.1 MPa, $T = 773-873$K), the average lifetime of peroxide radicals ~ 1 s [2].

Therefore at high velocities of the gas flow and short lengths exhaust tract in modern GT unit, a part of H$_2$O radicals can be removed beyond the limits of combustion chamber and smokestack.

A part of H$_2$O can also take part in oxidizing processes NO $\rightarrow$ NO$_2$ along with atmospheric ozone, taking place in dissipating gas tail. All this provides a sufficient reason for revising the role of steam in NO$_X$emissions moisture suppression technologies, as well as putting certain corrections into development of exhaust systems and those designed for combusstion products diffusion in the atmosphere, and programs of GT unit (CCGT unit) control, based on steam injection into the combustion chamber.

### References