Kinetics of the nitrogen oxides reaction with coke carbon in a low-temperature swirl furnace process

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Abstract. The work is devoted to the increase of ecological parameters of organic fuel burning process in power boilers combustion chambers. The technological method of nitrogen oxides decomposition on the surface of carbon particles with the formation of environmentally safe carbon dioxide and molecular nitrogen in low-temperature swirl combustion is considered. A methodology, a mathematical model and a program for calculating the process of a fuel combustion under conditions of multiple circulation, with periodic return of fuel particles to zones with the initial concentration of oxygen, are developed. It is shown that the stepwise supply of the oxidizer to the flare leads to a decrease in the generation of toxic nitrogen oxides, the formation of reducing zones, and the decomposition of the formed nitrogen oxides on the surface of burning coke particles. It has been established that the amount of decomposed nitrogen oxides depends on the surface area of the reacting fuel particles, as well as the time of their stay in the swirl zone of the low-temperature swirl furnace. With the use of calculated results, emissions of nitrogen oxides of reconstructed boilers are reliably predicted.

1. Introduction

At present, for the production of electricity and heat, solid fuels are mainly burned in high-power pulverized-coal boilers [1–6], which have a number of drawbacks: with an increase in the unit capacity of the boiler, the dimensions, the metal consumption and the costs of fabrication and installation increase unnecessarily, harmful substances into the atmosphere, there are problems of slagging of heating surfaces. In addition, the organization of flaring requires relatively fine grinding of the fuel, which determines the presence of an expensive, difficult to operate and explosive dust preparation system.

An alternative to a pulverized-coal torch is the method of low-temperature swirl (LTS) combustion. The concept of LTS-method (LTS-technology) was proposed by Professor V.V. Pomerantsev at the Leningrad Polytechnic Institute [7] (now St. Petersburg Polytechnic University of Peter the Great) and has been further developed now [8–15].

The LTS method is based on the principle of organizing multiple circulation with respect to fuel particles with periodic return to zones with an initial concentration of oxygen. The organization of the swirl stream flows, is achieved by the interaction of burner air jets and air of lower blasting.

2. Model of fuel combustion and reaction of nitrogen oxides with coke carbon

The most complete burning of carbon particles in the LTS-combustion chamber can be described by a set of chemical reactions proposed by V.V. Pomerantsev and S.M. Shestakov [16].
The decomposition of nitrogen oxides on the coke carbon is accounted for by the reaction:

5. $2C + 2NO = N_2 + 2CO - 180.2 \text{kJ/mol.}$ (1)

The designations of the reactive components are adopted as follows: $O_2 - 1$; $CO_2 - 2$; $CO - 3$; $H_2 - 4$; $H_2O - 5$, and nitrogen oxides $NO - 6$ and nitrogen $N_2 - 7$.

The change in the rate constants of chemical reactions from temperature is governed by the Arrhenius relationship:

$$k_i = k_{0i}\exp[-E_i/(RT)],$$

the pre-exponential factor of the i-th reaction – through the "pole" S.M. Shestakova:

$$\lg k_{0i} = 0.2 \cdot 10^{-4}E_i + 2.$$ (3)

Research L.A. Vulisa, V.V. Pomerantseva et al. show that between the values of the activation energy of various reactions of carbon with $O_2$ and $CO_2$ for the same coke, there is the following relationship:

$$\begin{align*}
\frac{E_{C+O_2=CO}}{E_{C+O_2=CO_2}} &= 1.1, \\
\frac{E_{C+CO_2=2CO}}{E_{C+O_2=CO_2}} &= 2.2, \\
\frac{E_{C+H_2O=CO}}{E_{C+O_2=CO_2}} &= 1.6
\end{align*}$$ (4)

To take into account the mass transfer near the carbon surface, the "reduced boundary film" method was used [16].

To assess the degree of influence of the reaction $CO + O_2 = CO_2$ in the burning out of a carbon particle, the criterion of N.N. Semenova is used (Se), which characterizes the ratio of the flux of matter absorbed by the homogeneous reaction of afterburning $CO + O_2 = CO_2$, to its diffusion flux:

$$Se = \left(k_4\Delta^2/D\right)^{1/2},$$ (5)

where $k_4$ – reaction rate constant; $\Delta=\delta/\text{Nu}_0$ – thickness of the reduced boundary film, m; $D$ – diffusion coefficient, $m^2/s$.

As the speed of reactions $CO + O_2 = CO_2$ and $2H_2 + O_2 = 2H_2O$ increases, as well as the thickness of the boundary layer increases, oxygen is increasingly consumed to burn off $CO$ and $H_2$ within the reduced film. The following cases are possible:

1. Oxygen reaches the surface of the carbon particle. This scheme is called the "burning" boundary layer scheme. It occurs at relatively low temperatures and a small thickness of the boundary layer.

2. Oxygen does not reach the surface of the carbon particle, consuming to burn off $CO$ and $H_2$ within the reduced film. Such a scheme is called the "double burning" boundary layer scheme. It is possible at a high process temperature and the burning of large particles of fuel.

3. Within the given film only diffusion processes occur, and carbon monoxide and hydrogen leave the reduced film and burn in the gas stream. This case is called a circuit with a "non-burning" boundary layer. Such a scheme is typical for fine carbon particles in conditions of moderate temperatures, which is typical for pulverized-coal furnaces.

The combustion scheme of a carbon particle is determined using the N.N. Semenov criterion. At $Se \leq 0.4$, combustion of $CO$ and $H_2$ can be neglected within the reduced film, and the "non-burning" boundary layer scheme can be used to analyze the combustion process. For $0.4 < Se < 2.0$ – the scheme of the "burning" boundary layer. At $Se \geq 2.0$, the "double burning" boundary layer scheme is applied. In the case where $Se > 100$, a "double burning" boundary layer is used with the CO burn-out on the burning surface inside the reduced film [17].

Analysis of the combustion of natural solid fuel particles in the LTS furnace [18], as well as the calculations performed, showed that the combustion process proceeds in the intermediate region...
according to the scheme of the "double burning" boundary layer (Se > 100), (the case of "wet" gasification); (figure 1).

Figure 1. Distribution of partial pressures (a) and flows (b) of the components in the given film of coarse ash particle: 1 — O₂; 2 — CO₂; 3 — CO; 4 — H₂; 5 — H₂O; 6 — NO; 7 — N₂; the "0" indexes — particle surface; "Δ" — flow

Carbon coke under this scheme burns out due to the reduction reactions

\[ \text{C} + \text{CO}_2 = 2\text{CO} \]
\[ \text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2 \]
\[ 2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O} \]
\[ 2\text{C} + 2\text{NO} = \text{N}_2 + 2\text{CO} \]

Reactions that go without changing the volume for the case under consideration:

\[ \begin{align*}
3. \quad & \text{C} + \text{CO}_2 = 2\text{CO} \\
3'. \quad & \text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2 \\
4'. \quad & 2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O} \\
5. \quad & 2\text{C} + 2\text{NO} = \text{N}_2 + 2\text{CO}
\end{align*} \]

The flux of carbon from the surface of the particle, taking into account the stoichiometric relationships:

\[ G_c = G_{20} + 1/2 G_{50} + 1/2 G_{60}. \]  

Expressions for partial pressures on the particle surface and component flows:

\[ p_{\text{CO}_2,0} = \frac{p_{\text{CO}_2,\Delta}}{1 + (k_3 \cdot \Delta / D)}; \quad g_{\text{CO}_2,0} = \frac{\alpha_D}{RT} N_3 p_{\text{CO}_2,\Delta} \]

\[ p_{\text{H}_2\text{O},0} = \frac{p_{\text{H}_2\text{O},\Delta} + 2p_{\text{O}_2,\Delta}}{1 + N_3}; \quad g_{\text{H}_2\text{O},0} = \frac{\alpha_D}{RT} N_3 p_{\text{H}_2\text{O},\Delta} + 2p_{\text{O}_2,\Delta} \]

\[ p_{\text{NO}_0} = \frac{p_{\text{NO},\Delta}}{1 + (k_5 \cdot \Delta / D)}; \quad g_{\text{NO}_0} = \frac{k_5}{RT} p_{\text{NO},\Delta} = \frac{k_5}{RT} \]

The flow of carbon from the particle surface, (kmol/(m²·s)):

\[ G_c = \frac{\alpha_D}{RT} \left[ \frac{N_3}{1 + N_3} p_{\text{CO}_2,\Delta} + \frac{N_5}{1 + N_5} \left( p_{\text{O}_2,\Delta} + 0.5p_{\text{H}_2\text{O},\Delta} \right) + \frac{N_5}{1 + N_5} p_{\text{NO},\Delta} \right]. \]
3. Results of a numerical study of a low-temperature swirl furnace process

Calculations of the combustion process were carried out with reference to the combustion of milling peat in the boiler BKZ-210 (Figure 2), and the incineration of wood waste – hydrolytic lignin, in the boiler TP-35U (Figure 3).

![Figure 2. Boiler BKZ-210 for burning milling peat](image1)

![Figure 3. Boiler TP-35U for burning of hydrolytic lignin](image2)

The reacting particles motion trajectories in the LTS furnace in a known velocity field are obtained by numerically solving equation (12), which takes into account the influence of two main forces-the forces of aerodynamic drag and gravity:

\[
m \frac{d\vec{V}}{d\tau} = \sum_{i=1}^{k} F_i + (\overline{W_f} - \overline{V}) \frac{dm}{d\tau}.
\]  

Comparison of the calculated and experimental trajectories of particles in the LTS furnace of the BKZ-210 boiler showed their good agreement [19, 20].

The concentrations of the main reactive components for calculating the combustion process (system 6) were taken to be typical of LTS furnaces [21, 22].

As a result of fuel burnup calculations (milling peat and hydrolytic lignin) in the LTS furnace (Figure 4), the concentrations of nitrogen oxides along the combustion chamber section were determined (Figure 5), taking into account the decomposition of nitrogen oxides on the circulating coke particles surface. The concentrations obtained on the average are lower by 30 %, in comparison with the combustion of the same fuels according to the scheme of the direct-flow pulverized-coal torch [23]. Thus, low-temperature swirl combustion can be considered as a promising technological method for reducing emissions of nitrogen oxides into the atmosphere during boiler operation.
Figure 4. Trajectories of burning particles motion in the LTS furnace:
   a) – boiler BKZ-210; b) – boiler TP-35U

Figure 5. Concentrations of nitrogen oxides in the LTS furnace:
   a) – boiler BKZ-210; b) – boiler TP-35U
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