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Selection of the optimal kinetic scheme for the formation of nitrogenous substances in the simulation of low-quality coal combustion

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The methods used to reduce emissions of harmful substances (mainly nitrogen oxides) at the moment still do not meet environmental requirements and don't give the desired result. In this article, a study was carried out by methods of 3D computer modeling of mass transfer processes using the example of low-quality coal combustion in the furnace chamber of a real heat-power facility. The choice of the kinetic model of the formation of nitrogenous substances is important for determining the most realistic scheme of the technological process of fuel combustion. The novelty of the proposed work is that in order to choose the optimal chemical model, two kinetic schemes for the formation of NO are considered, these are the Mitchell Tarbell model and the De Soete model. As a result of the conducted computational experiments, the high efficiency and adequacy of the Mitchell Tarbell kinetic model was noted in relation to the high-ash coal under study. This allows to conclude that the use of the Mitchell Tarbell model to reproduce the process of burning low-grade coals is preferable. The results obtained will help to realistically estimate the amount of NO emissions, as well as to design and implement various approaches to their minimization.

Keywords: emissions, 3D computer modeling, kinetic model, nitrogenous substances, low-grade coal

INTRODUCTION

Global coal consumption will hit a record high this year, the International Energy Agency (IEA) predicts. The world is close to the peak of fossil fuel use, and coal will be the first to be reduced, but we have not yet reached this. Despite the fact that the leading countries of the world announce their plans for 2020-2060 about achieving carbon neutrality, the rate of coal production does not seem to decline (Fig. 1).

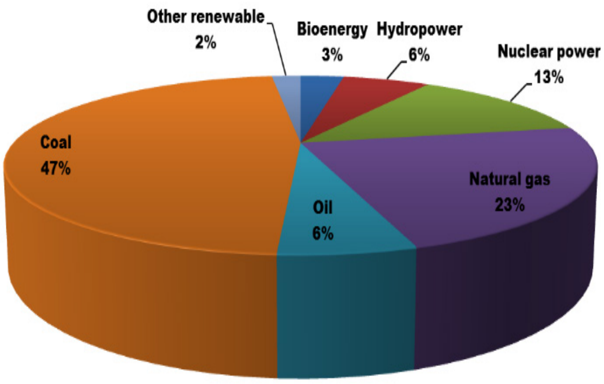

Fig. 1. World consumption of fuel resources

Demand for coal remains unwavering and is likely to hit record highs this year, pushing up global emissions. Top 10 countries by coal reserves: USA, Russia, China, Australia, India, Germany, Ukraine, Kazakhstan, South Africa, Indonesia. Top 10 countries by coal production: China, Indonesia, India, Australia, USA, Russia, South Africa, Kazakhstan, Poland, Colombia.

According to the World Energy Outlook (WEO) countries that have set targets for coal power phase-outs account for about 3% of global electricity generation. Unfortunately, in the first half of 2022 (H2), global coal consumption little changed (we estimate a decrease of less than 0.5%) compared with the first half of 2021 (H1), with the economic slowdown more than offsetting any demand increase resulting from higher natural gas prices (Fig. 2). For 2022, as a whole, WEO expects global coal demand to increase by 0.7% from 2021 to about 8 billion tons [1, 2].

In this term, WEO noted the two main aspects to phasing out coal in the energy sector: 1) stopping the construction of new power plants and 2) managing the reduction of emissions from existing assets.

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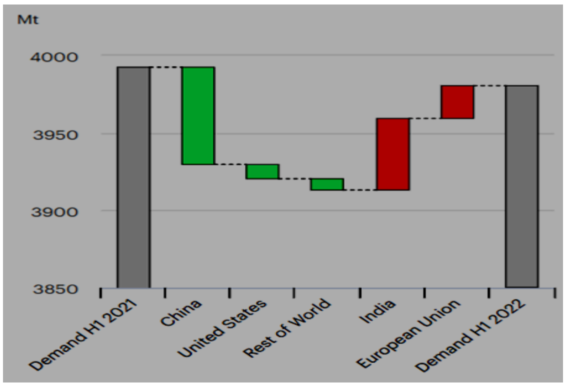

Fig. 2. Changes in global coal consumption by 2021-2022 (H1).

Advanced economies are seeing a faster phase-out of coal in the energy and industrial sectors. Demand will collectively decline by about 40% by 2030. This is due to climate policy and the rapid growth of renewable energy. Ensuring reductions in emissions from the existing fleet of coal-fired power plants is a major challenge for public policy. Given the dependence of a number of countries and regions on coal, the closure or conversion of coal mines and power plants can have serious economic and social consequences. Therefore, the use of coal, on the contrary, is expanding in many emerging markets and developing countries [2].

The thermal efficiency and environmental safety of energy enterprises is largely determined by the quality of the coals used. It is known that in developed countries (Germany, USA, etc.) only specially prepared fuel is burned, which is subjected to pre-enrichment, sorting, desulfurization, which certainly improves its quality [3-6].

In conditions of depletion of natural energy resources and environmental pollution, the rational use of energy fuel, increasing the efficiency of energy production and solving environmental problems are an urgent and important task that needs to be solved. The main energy fuel in Kazakhstan is coal. The poor quality of coal from the main Kazakh coal deposits leads to industrial and environmental problems during its operation. In this regard, studies of the processes of burning low-grade coals are relevant.

Conducting detailed and in-depth research in real conditions is much more expensive than conducting computational experiments using computer modeling methods. At the same time, the results obtained by computational methods can also ensure the development of effective technological solutions [7-9]. However, it is worth emphasizing here that the correct formulation of the problem in modeling plays a crucial role. Currently, there are various software packages and approaches being developed to obtain adequate and most realistic results. Unfortunately, there are no universal approaches yet. Therefore, it is important to consider and study each task separately, thereby at least grouping the main points.

THE CONSIDERED SCHEMES FOR THE FORMATION OF NITROGEN OXIDES

Combustion processes occur under conditions of strong turbulence and non-isothermal flow, multiphase medium with significant influence of nonlinear effects of thermal radiation, interphase interaction and multistage flow of chemical reactions. Such phenomena play an important role in the study of the natural phenomenon of low-grade coal burning [10-14]. All these factors must be taken into account in the formulation of the physical, mathematical and chemical model of the problem. A number of kinetic schemes based on global reaction rates have been developed to describe the processes of formation and destruction of nitrogen oxides [15, 16].

The choice of the most optimal scheme for the formation of nitrogen oxides during the combustion of low-grade pulverized coal fuel will provide adequate research results. This will give a chance to really estimate the amount of nitrogen oxide emissions, as well as to design and implement various approaches to minimize it. In the process of burning coal, nitrogen oxides are formed during homo- and heterogeneous reactions of air, volatile substances and charcoal. Nitrogen oxides occur in combustion gases in the form of NO, N_2O, and NO_2 compounds. Fig. 3 shows a simplified diagram of the mechanism of their formation.

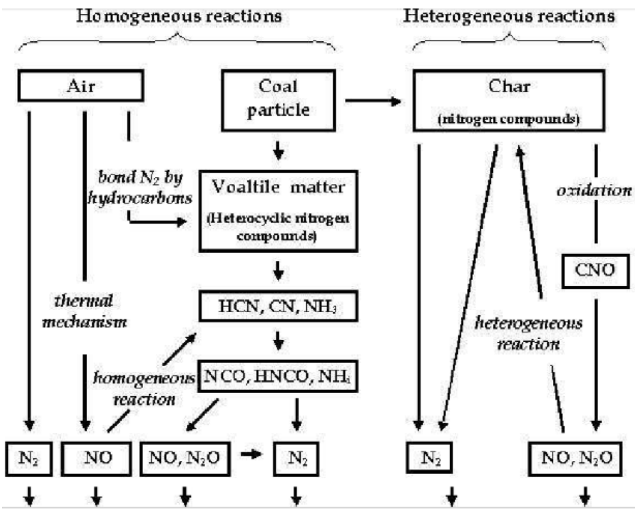

Fig.3. A simplified diagram of the mechanism of NOx formation

The complex mechanisms of nitrogen oxide formation during coal combustion are classified using a nitrogen source and divided into two main groups:

- fuel processes: oxidation of nitrogen compounds that are chemically bound to the organic matter of the fuel;
- thermal processes: reactions of atmospheric nitrogen with atomic oxygen, which is formed at high temperatures.

Nitrogen associated with coal (fuel) is released during the removal of volatile components. A portion of the nitrogen is rapidly converted to HCN, and the remainder of the fuel nitrogen reacts to form NH_3. These two species react and produce either NO or N_2, depending on local conditions. The NO formed can be reduced by a heterogeneous reaction with carbon particles. Global reaction rates are usually measured under controlled conditions over the temperature range of interest and are applicable to both high fuel and low fuel conditions. Various values for global reaction rates have been proposed by De Soete, Mitchell and Tarbell, *et al*.

In the proposed article, the processes of formation of nitrogen oxides are considered, according to two kinetic models of their formation – the Mitchell Tarbell model and the De Soete model. De Soete was the first researcher to develop a heterogeneous model of the formation and decomposition of NO and N_2O based on surface reactions with active sites [CN] and [CNO]. De Soete model is based on ten NO and N_2O production and reduction reactions:

$O_2 + 2[C] \rightarrow 2[CO]$ (R.1)
$[CO] \rightarrow CO + C_f$ (R.2)
$2[CO] \rightarrow CO_2 + [C] + C_f$ (R.3)
$O_2 + [C] + [CN] \rightarrow [CO] + [CNO]$ (R.4)
$[CNO] \rightarrow NO + [C]$ (R.5)
$NO + [C] \rightarrow 0{,}5\ N_2 + [CO]$ (R.6)
$[CN] + [CNO] \rightarrow N_2O + 2[C]$ (R.7)
$N_2O + [C] \rightarrow N2 + [CO]$ (R.8)
$NO + 2[C] \rightarrow [CO] + [C \ldots N]$ (R.9)
$2[C \ldots N] \rightarrow N_2 + 2[C]$ (R.10)

The disadvantage of this model is the lack of diffusion in the pores. However, at temperatures above 800 K, the formation of NO and N_2O is controlled by the diffusion of oxygen in the pores of the coal. At the same time, the probability of obtaining accurate results of modeling nitric oxide emissions from coal combustion without previous experiments is low.

In the case of coal combustion, the Mitchell Tarbell kinetic model of fuel NO formation takes into account coal pyrolysis, homogeneous combustion of hydrocarbons and heterogeneous coke burning. The general reaction mechanism used in the kinetic model is given below:

a) $C(s) + ½\ O_2 \rightarrow CO$ (R.1)
b) $NC(S) + ½\ O_2 \rightarrow NO$
$CO + ½\ O_2 \rightarrow CO_2$ (R.2)
$VM(s) \rightarrow C_mHB$ (R.3)
$C_mHB + O2 \rightarrow mCO + H_2$ (R.4)
$NC(s) \rightarrow HCN$ (R.5)
$NH_3 + O_2 \rightarrow NO + H_2O + H_2$ (R.6)
$NH_3 + NO \rightarrow N_2 + H_2O + H_2$ (R.7)
$N_2 + O_2 \rightarrow 2NO$ (R.8)
$HCN + H_2O \rightarrow NH_3 + CO$ (R.9)
$NO + C_mHB + H_2 \rightarrow HCN + H_2O$ (R.10)
$C(s) + NO \rightarrow CO + N_2$ (R.11)
$H_2 + ½\ O_2 \rightarrow H_2O$ (R.12)

Coal pyrolysis is described by R.3 and R.5, coal combustion - by R.1a, combustion of hydrocarbons formed in the process of the release of volatile coal components, is described by R.2, R.4 and R.12. R.8 - describes the mechanism of formation of thermal NO. The mechanism of formation of fuel NO is presented in R.1b, R.6, R.7 and R.9-11.

THE BASICS OF COMPUTATIONAL EXPERIMENTS AND RESULTS

To conduct computational experiments in the simulation of low-quality coal combustion, the FLOREAN software package [17-19] was used, which is based on solving conservative equations for the gas-fuel mixture using the control volume method.

The computer software package consists of a sub-model of the balance of momentum, energy, matter components, *k-ε* turbulence model, SIMPLE pressure correction method, six-stream thermal radiation model. This software package has been used to calculate flows in the combustion chambers of many thermal power plants both abroad and in Kazakhstan [20-26].

Based on the kinetic mechanism of the formation of nitrogen oxides NO_x according to the models of De Soete and Mitchell-Tarbell, computational experiments were carried out to determine the concentration characteristics of the formation and destruction of nitrogen oxides (NO and NO_2) in the furnace chamber of the boiler BKZ 75 Shakhtinskaya CHP when burning high-ash Kazakh coal (see the characteristics of Karaganda coal in Table 1) in it.

Table 1. Characteristics of Karaganda coal

Name	Value
Grinding fineness (R_{90}), *%*	20
Density of coal, *kg/m^3*	1350
Heat of combustion of coal, kJ/kg	$3.4162 \cdot 10^4$
Heat of combustion of coke, kJ/kg	$3.2814 \cdot 10^4$
A^c, %	35.10
$V^г$, %	22.00
W^P, %	10.60
C, %	79.57
H_2, %	6.63
O_2, %	9.65
S_2, %	1.92
N_2, %	2.23

Figs. 4 and 5 show a plot of the distribution of maximum, minimum and average values of nitric oxide NO concentration over the height of the combustion chamber for two models of NO_x formation.

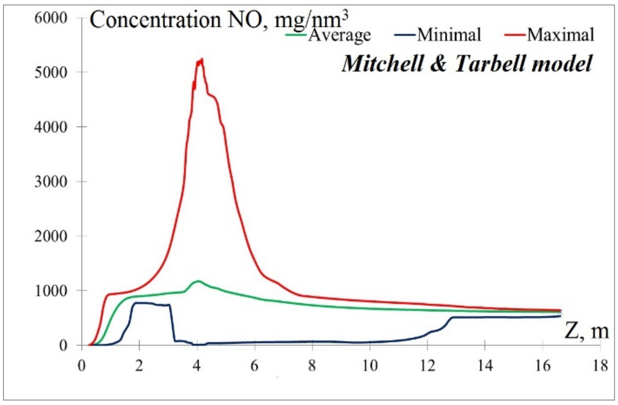

Fig. 4. Distribution of nitrogen oxide NO concentrations along the height of the combustion chamber of the BKZ-75 boiler for the NO formation model according to the Mitchell & Tarbell model

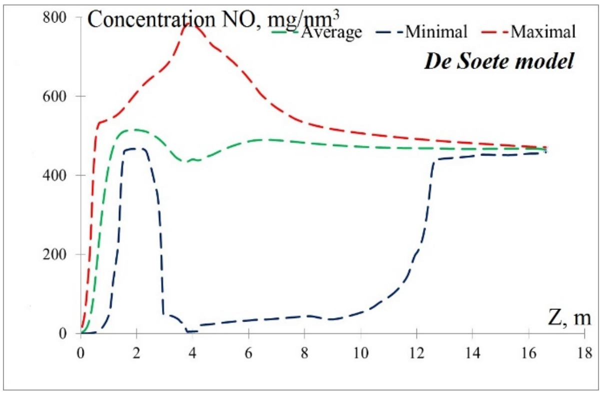

Fig. 5. Distribution of nitrogen oxides concentrations NO along the height of the combustion chamber of the BKZ-75 boiler for the NO formation model according to the De Soete model

An analysis of the graphs shows that the distribution curves of NO concentrations calculated using different models of their formation differ not only quantitatively, but also qualitatively. This is due to the fact that in the De Soete model, the calculation is made mainly in strict dependence on the oxygen concentration in the oxidizing medium. Also, the De Soete model is not sensitive enough to temperature changes at high temperatures, which affects the final results.

It can be seen that according to the Mitchell-Tarbell model, we have higher values of NO concentration compared to the De Soete model. So, at the outlet, the concentration of NO is equal to 606.14 mg/nm^3 (Fig. 4) and equal to 467.6 mg/nm^3 (Fig. 5). The difference in NO concentrations is significant and amounts to almost 23%.

The maximum concentrations of nitric oxide NO in the area of burners are associated with the oxidation of nitrogen N in the composition of the fuel (volume content 2.23%) and nitrogen N in the air (volume content ~ 77%), which enter here into the combustion chamber through the burners.

Figs. 6 and 7 show the results of three-dimensional distributions of nitric oxide NO concentrations in the furnace volume in the cross-section in the area of the burners: Z=3.98 m according to two models of NO_x formation (Mitchell-Tarbell and De Soete). From the analysis of the figures, it can be noted that the distribution of the concentration of nitric oxide NO in both models of NO_x formation for the selected section of the combustion chamber has a relative symmetry.

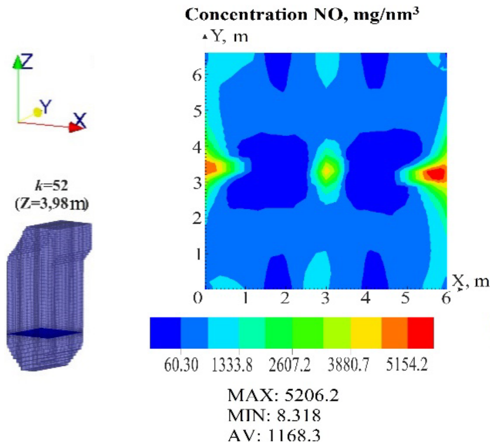

Fig. 6. Three-dimensional distribution of the concentration of nitrogen oxides NO in the cross-section (Z = 3.98m) of the combustion chamber of the BKZ-75 boiler for the NO_x formation model according to the Mitchell-Tarbell model

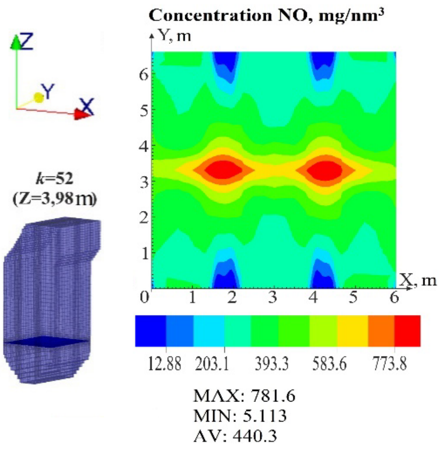

Fig. 7. Three-dimensional distribution of the concentration of nitrogen oxides NO in the cross section (Z = 3.98m) of the combustion chamber of the BKZ-75 boiler for the NO_x formation model according to the De Soete model

From the analysis of the distributions of the concentrations of nitrogen oxides NO in this section for both cases, it can be seen that they differ significantly (Figs. 6 and 7). The values of NO concentrations calculated according to the Mitchell-Tarbell model are higher everywhere in this section (average value is 1168 mg/nm^3) than the values of NO concentrations calculated according to the De Soete model (average value is 440 mg/nm^3).

The results of the distribution of NO concentrations calculated using the De Soete model (Fig. 7) are associated with a more idealized kinetic mechanism of this model, which is not sensitive enough to changes in temperature fields at high temperatures. As for the Mitchell-Tarbell model, it should be noted that it takes into account such factors as the size and composition of fuel particles, the degree of oxidation, changes in temperature fields, which, in turn, can have a significant impact on the processes of NO_x formation and distribution of NO concentrations in the sections of the combustion chamber.

A comparison of the results of the study using two models and field experimental data allows us to conclude that the Mitchell-Tarbell model is the most adequate describing model. From the analysis of the concentration fields of nitrogen oxides shown in Figs. 8 and 9, it can be noted that the results of calculating NO concentrations during computational experiments for the two models are significantly different.

From the distribution of the average concentrations of nitrogen oxide NO according to the results of the computational experiment, it was determined that the data of known field experiments are closer to the values obtained by the Mitchell-Tarbell model.

At the output, the average concentration of nitrogen oxide NO for the Mitchell-Tarbell model is 613 mg/nm^3, for the De Soete model is 463 mg/nm^3. At the same time, in the work, the experimental value (full-scale experiment at a thermal power plant) of the NO concentration at the output is 530 mg/nm^3.

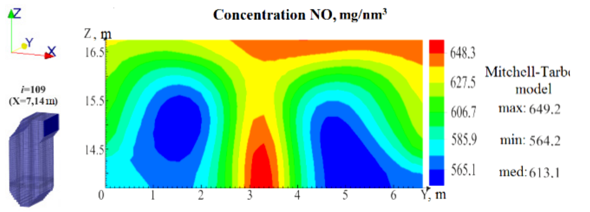

Fig. 8. Three-dimensional distribution of the concentration of nitrogen oxides NO in the longitudinal section at the outlet (X= 7 m) from the furnace chamber of the boiler BKZ-75 according to two models of NO_x formation

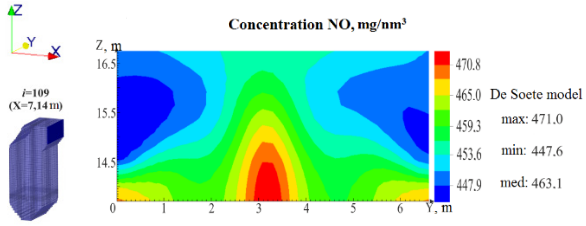

Fig. 9. Three-dimensional distribution of the concentration of nitrogen oxides NO in the longitudinal section at the outlet (X= 7 m) from the furnace chamber of the boiler BKZ-75 according to two models of NO_x formation

CONCLUSION

Based on the results of the work, the following conclusions can be drawn:

- Physico-chemical processes were studied during the combustion of high-ash energy fuel in the combustion chamber of an industrial energy facility, taking into account the main stages of coal combustion, the formation and destruction of harmful dust and gas emissions.
- A technique for 3D computer modeling of heat and mass transfer processes was developed, taking into account the kinetics of chemical reactions, multiphase and turbulent flow, nonlinear effects of thermal radiation during the movement of high temperature and chemically reacting flows in the combustion chambers of a thermal power plant.
- Physical, mathematical and chemical models of the problem were created that adequately describe the complex processes of physical and chemical transformations that occur during the combustion of high-ash Karaganda coal grade KR-200 in the combustion chamber of the BKZ-75-39FB boiler at Shakhtinskaya CHPP.

• Computational experiments were carried out to study the concentration characteristics of the components in the combustion chamber BKZ-75-39 using two kinetic models of the formation of nitrogen oxides NO_x (Mitchell-Tarbell and De Soete). It was established that the choice of models affects the formation of NO concentration fields. So, at the outlet of the combustion chamber, the calculated value of the NO concentration according to the Mitchell-Tarbell model is 613 mg/nm^3, and according to the De Soete model is 463 mg/nm^3. Comparison with the experimental data obtained at the CHPP showed that the results of the numerical calculation of the concentration fields of NO according to the Mitchell-Tarbell model are closer to the results of a full-scale experiment and to the MPC values for coal-burning TPPs.

Thus, as a result of the conducted computational experiments, the high efficiency and adequacy of the Mitchell Tarbell kinetic model was noted in relation to the high-ash coal under study. This allows us to conclude that the use of the Mitchell Tarbell model to reproduce the process of burning low-grade coals is more preferable. The results obtained will help to realistically estimate the amount of nitrogen oxide emissions, as well as to design and implement various approaches to their minimization.

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