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AVOGADRO PROGRAM: ENVIRONMENTAL PROBLEMS OF HEAT ENGINEERING

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Results of some studies of formation and transformation of harmful substances during combustion of organic fuels are presented. The studies were conducted within the framework of the program "Environmental Problems of Heat Engineering" of the AVOGADRO system.

Introduction. The automated AVOGADRO system [1], which is being developed at present, is aimed at the solution of the problem of informational provision of scientific studies in the field of physicochemical gasdynamics. Due to the fact that at present environmental problems are especially acute, a special program "Environmental Problems of Heat Engineering" was developed within the framework of the AVOGADRO system. The aim of the program is to develop recommendations on minimization of environmental consequences caused by discharge of pollutants into the atmosphere that result from operation of power plants and other objects of the power industry. The main directions of the program are the following:

- modeling of the process of combustion of solid, liquid, and gaseous fuels with formation of nitrogen and sulfur oxides, polycyclic aromatic hydrocarbons, and soot in various furnaces and combustion chambers;
- development of methods for suppressing the formation of harmful substances in combustion of organic fuels and also for purification of discharge gases of harmful impurities;
- study of the chemical composition and dynamics of plumes of thermoelectric plants in the atmosphere; modeling of processes causing formation of acid rain.

In what follows we present some results obtained within the framework of the program mentioned in which an important role is played by heat and mass transfer processes.

1. Formation of Fuel NO. A characteristic feature of kinetic processes in the initial section of a dust-coal plume, where discharge and combustion of volatile components take place, is the formation of fuel nitrogen oxides. As experimental data show, clearly defined flame combustion of volatiles near the surface of fuel particles is observed only with ignition of large coal particles having a size greater than 150 μm [2]. As the size of the particles decreases and the amount of volatiles that burn up per unit surface of the flame front increases, combustion of volatiles passes from a diffusive to a kinetic regime.

In [3] the mechanism of emission of fuel NO is considered. This mechanism involves the kinetics of emergence of volatiles from coal with formation of a combustible gas mixture and the kinetics of chemical reactions in the gas phase, which describes the transition of nitrogen-containing compounds to NO during combustion of volatiles. However, due to the large dimensionality and the clearly defined rigidity of the kinetic scheme obtained, its realization within the framework of two- or three-dimensional schemes of calculation of turbulent combustion in real combustion chambers runs into great computational difficulties. On the other hand, as is shown in [3], the assumption of a purely kinetic regime of combustion of volatiles near a coal particle, even for small coal particles, is insufficiently correct, and to correctly describe this process it is necessary to include into consideration a diffusive mechanism of oxidant supply into the combustion zone, thus leading to even more complication of the problem.

Due to the aforesaid, development of simplified kinetic models of NO formation that are based on global (generalized) kinetic schemes is of considerable interest. These models join well with a general scheme of

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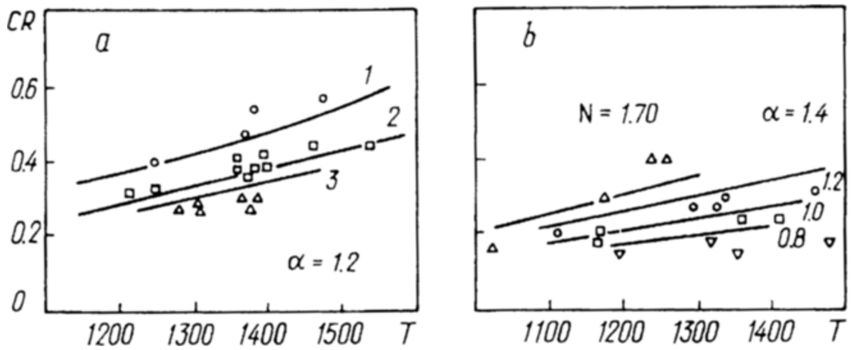


Fig. 1. Dependence of the degree of conversion CR of fuel N to NO on the temperature and the content of N in the coal for a concentration of O_2 in the air of 25 wt.% (a) and on the temperature and the excess air α for an O_2 concentration in the air of 23 wt.% (b). N content in the studied coals (% on dry ash-free mass): 1) 0.94, 2) 1.70, 3) 1.90. Points are experimental data [5]. T, °C.

mathematical simulation of furnace processes and can be used effectively in two- and three-dimensional calculations of burners and combustion chambers [4].

On the basis of processed experimental data [5] we obtained a global kinetic model of NO formation in a dust-coal plume. The dynamics of this process is described by a kinetic equation of the form

$$dy_{\mathrm{NO}}/dt = 2.82\cdot 10^7 \exp\left(-4530/T\right) y_{\mathrm{O}_2} y_{\mathrm{N}}\,,$$

where y_i is the concentration of the i-th component in the gas (mole/cm^3), y_{N} is the concentration of nitrogen in the fuel (mole/cm^3, the carrier gas). It is assumed that y_{N} is proportional to the degree of fuel conversion. This makes it possible to allow for the contribution of bound nitrogen of the coke residue to the overall emission of fuel NO.

The kinetic model is combined with a mathematical model of a dust-coal plume [6] that involves the ψ-ω procedure for determination of the velocity field of the carrier gas flow, the Euler approach to the description of coal particles, the kinetics of combustion of coal particles, and the k-ε model of turbulence. In Fig. 1 results of a calculation of the dependence of the degree of conversion of fuel N to NO on the process parameters are compared to experimental data [5].

2. Formation of NO in Combustion of Gaseous Fuel. The solution of the problem of combustion of hydrocarbon fuels in combustion chambers is associated with integration of the equations of gas dynamics simultaneously with the kinetic equations for the change in the concentrations of the chemical components. Here, as in combustion of coal dust, global kinetic schemes are used that include several basic stages of the process. The kinetic characteristics of these stages are determined experimentally in full-scale installations, which, on the one hand, makes it possible to allow for the effect of turbulence on the rate of the chemical reactions [7]; on the other hand, global kinetic schemes do not allow one to determine rather accurately the concentrations of the intermediate active components (atoms and radicals), which play a major role in the formation of toxic substances (nitrogen and sulfur oxides, polycyclic aromatic hydrocarbons, etc.). Therefore, in modeling processes of formation of toxic substances in combustion chambers it is important to use an optimum kinetic mechanism of the considered process (a kinetic model of the medium) that provides the correct behavior of the concentrations of the intermediate active components and involves the minimum number of components and elementary chemical reactions.

The solution of the problem of the choice of an optimal kinetic mechanism of the process is realized in the AVOGADRO system by means of the generator of kinetic models of the medium [8]. The concentrations of some components, the rate of their production, the gas temperature, etc. can serve as purpose functions according to which an optimal kinetic mechanism is chosen. A spatially uniform nonstationary problem, flow behind a shock wave front, in a flow tube, and in a jet, etc. can be trial problems in solving which an optimal mechanism is selected.

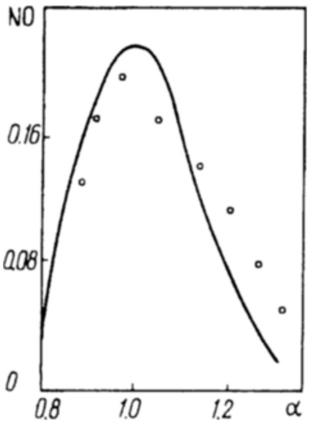


Fig. 2. Dependence of the NO concentration on excess air α in combustion of a prepared natural gas–air mixture in a combustion chamber. Points are experimental data [10]. NO, g/m^3.

Using the generator of kinetic models of the medium we obtained a number of optimum kinetic schemes as applied to the process of formation of toxic substances in combustion of a gas fuel in an axisymmetric combustion chamber.

The mechanism of NO formation in combustion of hydrocarbon fuels is determined by the reactions

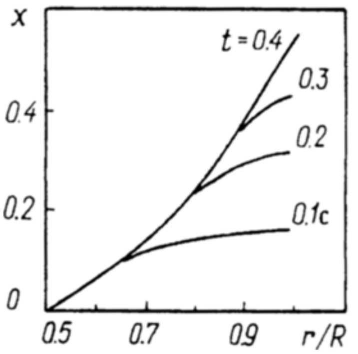
$$O + N_2 \rightarrow NO + N\,, \quad N + O_2 \rightarrow NO + O\,, \quad N + OH \rightarrow NO + H\,,$$

which form Zel'dovich's expanded mechanism. The rate of the process is specified by the first reaction, which has an activation energy of about 320 kJ/mole. Therefore, NO is generated very slowly even at rather high temperatures. Here, as calculations show, the usual assumption of partial equilibrium of atomic oxygen [9] in combination with a global kinetic scheme of hydrocarbon combustion give underestimated values of NO concentrations at the outlet from the combustion chamber. Calculations show that the rate of the process depends strongly on the level of gas temperatures in the combustion zone, the time of reaction, and the coefficient of air excess. In Fig. 2 results of a calculation of NO formation in the combustion chamber (the combustible mixture is natural gas with air) are compared to experimental data [10].

3. Binding of SO_2 by CaO Particles. Binding of SO_2 by limestone particles in combustion of solid fuel in combustion chambers is a promising direction in purification of flue gases of sulfur oxides. The mathematical models developed so far allow one to describe the basic parameters of the process only for monodisperse systems of particles [11]. In the present paper a more general polydisperse model is considered, by means of which characteristics of the process in real systems can be calculated.

When a limestone particle enters the combustion chamber it is calcined practically instantaneously ($CaCO_3 \rightarrow CaO + CO_2$). In a coal-dust plume this time is approximately equal to the period of volatilization of sulfur from the fuel and is about 0.1 sec [12]. Results of experimental studies show that during calcination porous particles of lime (CaO) are formed that consist of nonporous spherical grains of equal radii, which then increase in sulfurization of the grains (the molar volume of $CaSO_4$ is almost 3 times larger than the molar volume of CaO), thus decreasing the porosity of the lime particles [13]. The heterogeneous reaction involves the following physicochemical mechanisms: diffusion of SO_2 from the gas volume within a particle through pores between the grains; diffusion through the solid layer of $CaSO_4$ that forms on the surface of the grains; chemical reaction of CaO and SO_2 on the interface between CaO and $CaSO_4$ inside the grains. It is assumed that the reaction occurs with excess O_2.

The basic equations describing the process considered are obtained from the conditions of material balance written for the particles and the grains composing them. The polydisperse system of lime particles is divided into fractions according to size. It is assumed that the mean radius of the particles within a fraction does not change during sulfurization. At the time $t = 0$ the quantity of SO_2 in the gas and of CaO in each fraction is specified. For each fraction i the system of equations for finding the concentration of SO_2 inside a particle c_i and the change in the radius of the unreacted core of CaO in a grain as a function of the time [11] is solved. Numerical integration



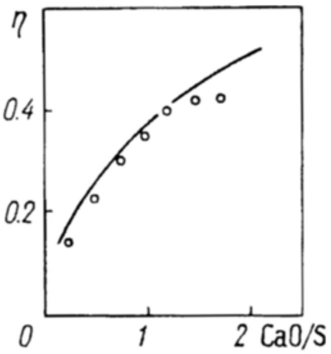


Fig. 3. Local degree of sulfurization of limestone particles with a diameter of 60 μm (process temperature 1050 K, mole ratio CaO/S = 1) as a function of time.

Fig. 4. Dependence of the degree of SO_2 removal on the mole ratio CaO/S (process temperature 1050 K, mean diameter of the particles 60 μm). Points are experimental data [14].

is performed until either the concentration of SO_2 in the gas volume or the porosity of the particle at its surface vanishes.

As an example the basic parameters of the process in coal-dust combustion with direct supply of limestone to the plume together with the fuel [14] are calculated. The size distribution of the limestone particles was described by the Rozin–Rammler law, and the mean diameter of particles was 60 μm. The temperature of the process was varied from 1000 to 1400 K. The mole ratio CaO/S was varied from 0.5 to 10. In Figs. 3 and 4 calculation results are presented and compared to existing experimental data. The time of attaining maximum sulfurization is about 0.4 sec.

4. Electron-Beam Purification of Gases of NO and SO_2. Purification of flue gases of thermoelectric plants of nitrogen and sulfur oxides is an important environmental problem. Flue gases of thermoelectric plants are characterized by relatively low concentrations of harmful substances contained in them (nitrogen and sulfur oxides) and by high flow rates. This makes their purification by ordinary methods difficult and is the reason for the fact that in the power industry, as compared to other industries, the situation concerning protection of the atmosphere from polution is the worst.

Recently, due to the development of new technologies and improvement of their efficiency new physicochemical methods have been suggested for purification of industrial gases of harmful discharges. At present the most effective and studied among them is the method of radiative treatment of gas by an electron beam [15]. The physicochemical processes occurring under the effect of an electron beam on a gas that contains sulfur and nitrogen oxides can be divided into the following groups: a) gas-phase processes induced by ionizing radiation; b) thermal processes caused by interaction between ammonia and SO_2; c) a gas–liquid phase transition; d) heterogeneous processes induced by ionizing radiation [16].

In [17] an optimum kinetic mechanism of radiative-chemical oxidation of NO and SO_2 in flue gases of thermoelectric plants was constructed. A kinetic scheme consisting of 740 reactions [18], supplemented by 21 reactions of formation of active components under the influence of ionizing radiation on the gas, was used as the initial set of reactions. The procedure of elimination of reactions from the kinetic scheme with a threshold of sensitivity of 20% in the concentrations of NO, SO_2, NO_2, and N_2O within the integration range over the absorbed dose of radiation from zero to 20 kGy allowed one to reduce the total number of reactions to 42.

Along with high-speed gas-phase reactions induced by ionizing radiation slower thermal reactions between SO_2 and NH_3 that cause additional reduction of the SO_2 concentration take place in the gas. The kinetic mechanism of the process was obtained in [17] on the basis of an analysis of available experimental data.

An important role in electron-beam purification of gases of nitrogen and sulfur oxides is played by heterogeneous processes on the surface of or inside particles of water aerosol that are introduced into the flow

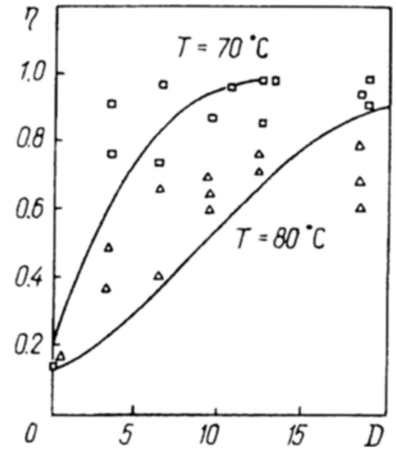


Fig. 5. Dependence of the degree of SO_2 removal on the radiation dose for different temperatures T at the reactor outlet. Gas humidity is 12%, initial content of SO_2 is equal to 1000 cm^3/m^3, NO = 300 cm^3/m^3, NH_3 = 2300 cm^3/m^3. Points are experimental data [21]. D, kGy.

through a system of nozzles [19]. The processes of heat and mass exchange between the aerosol particles and the surrounding gas, on the one hand, decrease the temperature of the flow and, on the other hand, increase the humidity of the gas. This intensifies both the gas-phase and liquid-phase chemical processes. The adopted kinetic scheme of liquid-phase oxidation of SO_2 in aerosol droplets was developed by the present authors on the basis of an analysis of available kinetic schemes of liquid-phase oxidation of SO_2 under atmospheric conditions [20].

A set of calculations was conducted using the obtained kinetic schemes of NO and SO_2 oxidation during the process of radiative action of fast electrons on the gas. The initial contents of NO and SO_2, the temperature of the process, the absolute humidity, the absorbed dose of radiation, and other parameters of the process were varied. Figure 5 compares results of calculation of SO_2 oxidation with test data [21]. Rather good agreement between the calculated and experimental data can be noted.

REFERENCES

1. A. A. Levitskii, S. A. Losev, and V. N. Makarov, Mathematical Methods in Chemical Kinetics [in Russian], Novosibirsk (1990), pp. 7-38.
2. V. I. Babii and Yu. F. Kuvaev, Combustion of Coal Dust and Calculation of a Coal-Dust Plume [in Russian], Moscow (1986).
3. G. Ya. Gerasimov, S. A. Losev, and V. N. Makarov, Informatics in Physicochemical Gas Dynamics [in Russian], Moscow (1992), pp. 39-46.
4. E. P. Volkov, L. I. Zaichik, and V. A. Pershukov, Simulation of Solid Fuel Combustion [in Russian], Moscow (1994).
5. K. Okazaki, M. Ohya, I. Yuri, and K. Ohtake, in: Coal Combustion: Science and Technology of Industrial and Utility Applications (ed. by J. Fend), New York (1988), pp. 821-828.
6. G. Ya. Gerasimov and E. V. Samuilov, Heat and Mass Transfer–MIF, Minsk, Vol. 10, 64-66 (1988).
7. H. A. Arbib, Y. Goldman, J. B. Greenberg, et al., Combust. Flame, 38, 259-270 (1980).
8. V. N. Makarov, Preprint No. 15-95, Institute of Mechanics of Moscow State University, Moscow (1995).
9. M. C. Drake, R. W. Pitz, S. M. Correa, et al., in: 20th Symp. (Int.) on Combustion, Pittsburgh (1984), pp. 1983-1990.
10. I. Ya. Sigal, Teploenergetika, No. 3, 5-10 (1983).
11. G. Silcox, D. M. Slaughter, and D. W. Pershing, in: 20th Symp. (Int.) on Combustion, Pittsburgh (1984), pp. 1357-1364.

12. F. F. Ots, Processes in Vapor Generators in Combustion of Schists and Kansk-Achinsk Coals [in Russian], Moscow (1977).
13. M. Hartman and R. W. Coughlin, AIChE J., **22**, 490-498 (1976).
14. N. A. Burdett, J. R. P. Cooper, S. Dearnley, et al., J. Inst. Energy, **58**, 64-69 (1985).
15. E. V. Samuilov, G. Ya. Gerasimov, M. V. Faminskaya, et al., Teploénergetika, No. 8, 64-68 (1989).
16. G. Ya. Gerasimov, T. S. Gerasimova, I. P. Tokmacheva, et al., Khim. Vysok. Énergii, **25**, No. 2, 99-104 (1991).
17. G. Ya. Gerasimov, T. S. Gerasimova, V. N. Makarov, et al., Khim. Vysok. Énergii, **30**, No. 1, 34-38 (1996).
18. H. Matzig, Chemical Kinetics of Flue Gas Cleaning by Electron Beam, KFK 4494, Kernforschungszentrum, Karlsruhe (1989).
19. A. N. Yermakov, B. M. Zhitomirsky, D. M. Sozurakov, et al., Radiat. Phys. Chem., **45**, 1071-1076 (1995).
20. R. E. Huie and P. Neta, Atmospheric Environment, **21**, 1743-1747 (1987).
21. N. Frank, S. Hirano, and K. Kawamura, Radiat. Phys. Chem., **31**, 57-82 (1988).