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Simulation of Parameters of Submicron Particles Formed in Combustion Products of Coals

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Abstract—Thermodynamic analysis of the composition of combustion products have been performed for 15 types of coals with and without allowance for potassium and sodium aluminosilicates. Based on the results obtained, a closed model has been proposed for the formation of submicron particles in the combustion products of the coals, which enables one to obtain the upper estimate for the content of submicron particles in these products. The bulk condensation of potassium sulfate vapor in the flow of the combustion products and upon their cooling along a technological path has been numerically simulated by means of computer-assisted realization of the proposed model. The number concentration and size distribution of the formed particles have been determined. Agreement with experimental data on the average particle size has been reached at a reasonable value of a free parameter of the model.

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INTRODUCTION

The presence of highly dispersed particles in the atmosphere is ecologically hazardous [1], and this circumstance has been reflected in the limitations on the concentration of particles of the $PM_{2.5}$ class, i.e., particles with sizes smaller than 2.5 μm, in the United States National Ambient Air Quality Standards (NAAQS). One of the sources of the aforementioned type of atmospheric pollution is the emission of submicron particles upon combustion of coals. In this case, the hazard is relevant to not only the particles themselves, but also various hazardous substances that can be adsorbed on their surface, e.g., some toxic trace elements contained in coals [2–4]. The bulk condensation of vapors of substances produced from the mineral moiety of coals during combustion (through the "solid–vapor–particle pathway") is a probable formation mechanism of submicron particles [5–7]. For efficient trapping of the above-mentioned particles, it is necessary to know the parameters of condensation aerosols that result from combustion, such as their number concentration and size distribution, which can be used for numerical simulation of the bulk condensation process. As applied to the combustion products of coals, which are multicomponent reactive systems, it is reasonable to use a comprehensive thermodynamic and kinetic approach [8]. According to this approach, the compositions of the gaseous and condensed phases and the order of condensation of different substances in the course of cooling the combustion products along a technological path are determined at the first stage by the methods of chemical thermodynamics (see Fig. 1). The desired parameters of a condensation aerosol are found at the second stage by solving the kinetic equation of bulk condensation with allowance for the results of the thermodynamic analysis.

Combustion products of 15 types of power-generating coals from different deposits of Russia and some other countries were the objects of this study. Substances that are evaporated at furnace temperatures during coal combustion and, then, being cooled, form submicron particles of flue ash as a result of bulk condensation are of interest from the point of view of studying the mechanism of the formation of highly dispersed ash carryovers. Potassium and sodium are among the most volatile ash-forming elements.

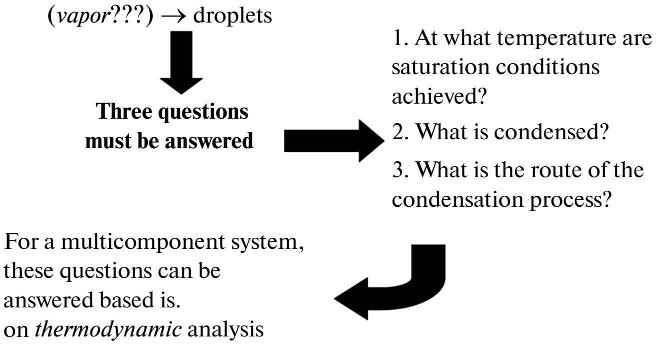

Fig. 1. Schematic representation of the comprehensive approach to simulation of bulk condensation in a multicomponent reactive system. Stage I.

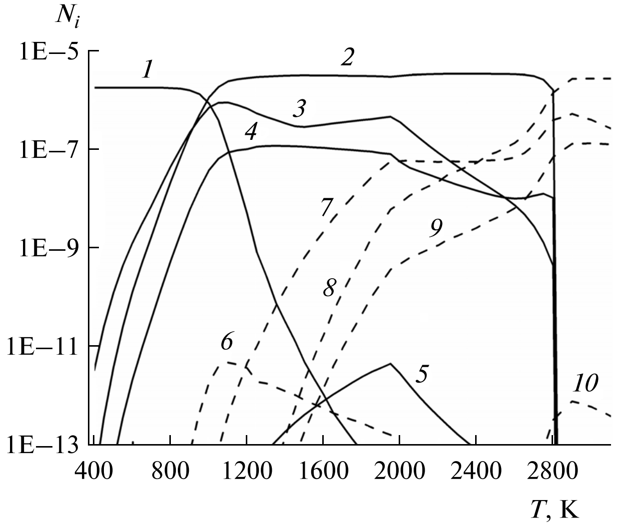

Fig. 2. The amounts of potassium-containing components (moles) in combustion products of Donetsk coal (with allowance for potassium aluminosilicates): (*1*) K_2SO_4*, (*2*) $KAlSi_2O_6$*, (*3*) $KAlSi_3O_8$*, (*4*) $KAlSiO_4$*, (*5*) $K_2Si_3O_3$*, (*6*) K_2SO_4, (*7*) KOH, (*8*) K, (*9*) KO, and (*10*) K_2O. Dashed and solid lines refer to gaseous and condensed phases, respectively. Asterisks denote components in the condensed phase.

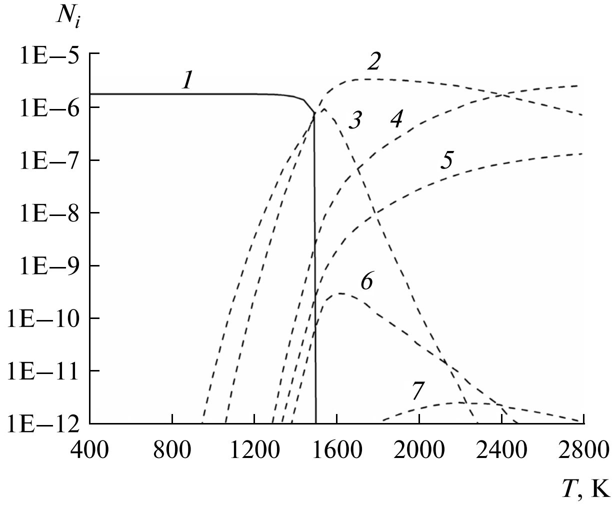

Fig. 3. The amounts of potassium-containing components (moles) in combustion products of Donetsk coal (with no allowance for potassium aluminosilicates): (*1*) K_2SO_4*, (*2*) KOH, (*3*) K_2SO_4, (*4*) K, (*5*) KO, (*6*) $K_2O_2H_2$, and (*7*) K_2O. Dashed and solid lines refer to gaseous and condensed phases, respectively. The asterisk denotes that the component is in the condensed phase.

Therefore, they were selected for the thermodynamic analysis of the formation and condensation of vapors of such elements and compounds thereof upon coal combustion.

Coals of the Berezovskaya, Kuznetsk, Pechora, Moscow oblast, Donetsk (Ukraine), and Ekibastuz (Kazakhstan) basins, as wall as coals of Khabarovsk krai, Chukotka, and the Republic of Sakha (Yakutia) [9] and four types of Chinese coals (see [5]), were selected for the investigation. It should be noted that the compositions of the coals varied in wide ranges (%): ash, 5.57–48.0; sulfur, 0.3–6.5; potassium, 0.4–3.5; and sodium, 0.2–1.9.

STAGE I. THERMODYNAMIC ANALYSIS

The composition of coal combustion products as depending on temperature was calculated using the modified TETRAN computer program, developed under the direction of one of the authors (E.V. Samuilov). The program realizes the method of calculating the composition and properties of multiphase reactive systems [10]. The necessary information on the thermodynamic properties of individual substances was taken from [11–13]. Altogether, 194 substances formed from atoms of 14 elements were taken into account in the calculations. Taking into account the data presented in [14], the calculations were performed for a four-phase system composed of a gaseous phase and three condensed phases in different variants that took into account potassium and sodium aluminosilicate alone, alkali metal sulfates alone or chlorides alone, and mixed systems comprising all of these compounds. This approach enabled us to consider the entire temperature range of the passage of potassium and sodium compounds to the gaseous phase. Excess coefficient of the oxidant (air) was taken to be 1.2. The results of the thermodynamic analysis as applied to the considered coals have been partly reported in another of our works [15].

In accordance with the calculated data (Figs. 2, 3; Table 1), for the majority of coals containing potassium and sodium in the form of aluminosilicates, these elements may be present in the gaseous phase at temperatures above the furnace ones. As has been established in [16], the main factor affecting the temperature of the passage of potassium and sodium compounds to a condensed phase is the Ca/Si ratio. Coals with Ca/Si < 1 are characterized by substantially higher temperatures of existence of these elements in gaseous forms than coals with Ca/Si > 1. Of all the considered coals, only coals from the Beresovskaya opencast and Yanzhou deposit (China) have a Ca/Si ratio >1, and the composition of the mineral moiety of the coals has almost no effect on the passage of potassium and sodium compounds to the gaseous phase. In this case, they can form gaseous compounds at temperatures of ≈1250–1500 K (potassium) and ≈1050–1350 K (sodium), the vapors of which are mainly condensed upon cooling in the form of sulfates. The results obtained agree with the experimental data reported in [5], according to which sulfates of alkali metals represent the main components of ash carryover with a particle size of 0.06 μm. Note that the con-

Table 1. Temperatures of the passage of potassium and sodium compounds to the condensed phase in combustion products of considered coals with allowance (with) and with no allowance (without) for potassium and sodium aluminosilicates

No.	Coal	Ca/Si	Potassium with	Potassium without	Sodium with	Sodium without
1	Krasnoyarskugol', Beresovskii opencast, RF	1.5	1250	1250	1300	1050
2	Kyznetsk basin, CC2CCPOKI, RF	0.1	2650	1400	1850	1150
3	Kyznetsk basin, Mokhovskoi opencast, RF	0.72	1850	1350	1600	1100
4	Kyznetsk basin, Mokhovskoi opencast, RF	0.77	1600	1250	1650	1100
5	Pechora basin, Vorkutinskaya mine, RF	0.06	2800	1400	1950	1150
6	Moscow region basin, Novomoskovskaya mine, RF	0.11	2600	1350	1700	1050
7	Khabarovsk krai, Urgal'skoe deposit, RF	0.04	2700	1300	2000	1100
8	Chukotka, Bukhta Ugol'naya deposit, RF	0.128	2550	1350	1850	1150
9	Republic of Sakha, Neryunginskoe deposit, RF	0.10	2550	1300	1800	1100
10	Donetsk basin, A, shtyb, SSh, Ukraine	0.06	2800	1500	1950	1350
11	Ekibastuz basin, Kazakhstan	0.028	2800	1400	1850	1100
12	Yanzhou, Cina	1.4	1300	1300	1300	1050
13	YZLS, Cina	0.22	2050	1350	1600	1050
14	Baotou, Cina	0.447	1800	1300	1550	1050
15	Wangfg, Cina	0.15	2400	1300	1700	1050

densation temperature of potassium compounds is higher than that of sodium compounds (see Table 1). Therefore, potassium sulfate condensation was considered at the next stage. It was assumed that the formed potassium sulfate particles would play the role of condensation nuclei for other evaporated substances upon cooling of combustion products in a technological path.

STAGE II. KINETIC ANALYSIS

At the next (kinetic) stage of the study, a stationary one-dimensional flow of combustion products in a channel with a constant cross section at a constant rate and a preset axial temperature gradient, which simulates cooling of combustion products in a technological path, was considered. The model used for the formation process of submicron particles in coal combustion products comprised the following features:

(1) formation of a condensable component (potassium sulfate) in the gaseous phase under the approximation of a thermodynamic equilibrium without allowance for aluminosilicates; and

(2) formation of a condensation aerosol of potassium sulfate with account of the process kinetics.

This model that takes into account the formation of aluminosilicates provides the upper estimate for the content of submicron particles in the coal combustion products.

The driving force of the condensation process is the excess partial pressure of a condensing component relative to the equilibrium value at a given temperature, with the excess pressure being characterized by the degree of supersaturation. As applied to the case under consideration, the degree of supersaturation may be written in the following form:

$$s = \frac{N_{K_2SO_4}}{N^s_{K_2SO_4}}. \qquad (1)$$

Here, $N_{K_2SO_4}$ is the current number of moles of potassium sulfate in the gaseous phase corresponding to the one-phase (upon frozen condensation) thermodynamic equilibrium in the gaseous phase (analog of partial vapor pressure) and $N^s_{K_2SO_4}$ is the number of moles of potassium sulfate in the gaseous phase corresponding to the two-phase thermodynamic equilibrium in the system (analog of saturation vapor pressure). At each step of the numerical simulation bulk condensation kinetics, the degree of supersaturation was calculated as follows. The following temperature dependence was obtained for the denominator of Eq. (1) from the calculated data of the first stage (see Fig. 4):

$$\log N^s_{K_2SO_4} = A^s - B^s/T, \qquad (2)$$

where $A^s = 4.42991$ and $B^s = 1.55904 \times 10^4$. In order to determine the numerator of Eq. (1), the following set of two equations—the law of mass action and material balance—was written for the main potassium-containing components (KOH and K_2SO_4) of the gaseous phase upon frozen condensation in the temperature range under consideration:

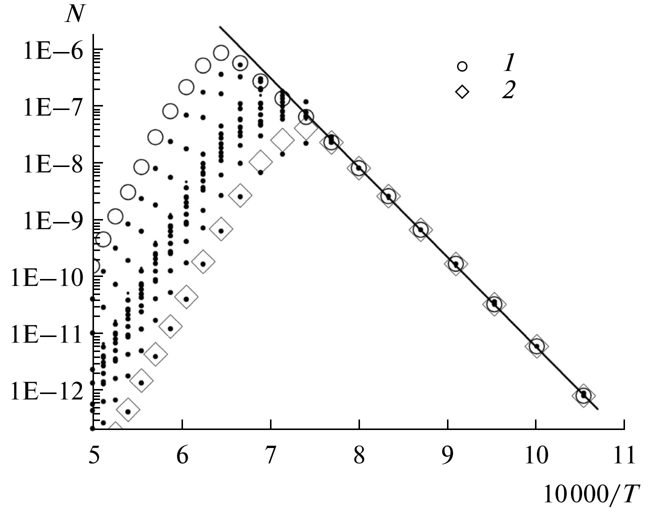

Fig. 4. Temperature dependence of the amount of K_2SO_4 (moles) in the gaseous phase of combustion products of coals from (*1*) Donetsk and (*2*) Kuznetsk deposits. Filled dots denote the data on all other coals under consideration. The solid line shows two-phase thermodynamic equilibrium for potassium sulfate.

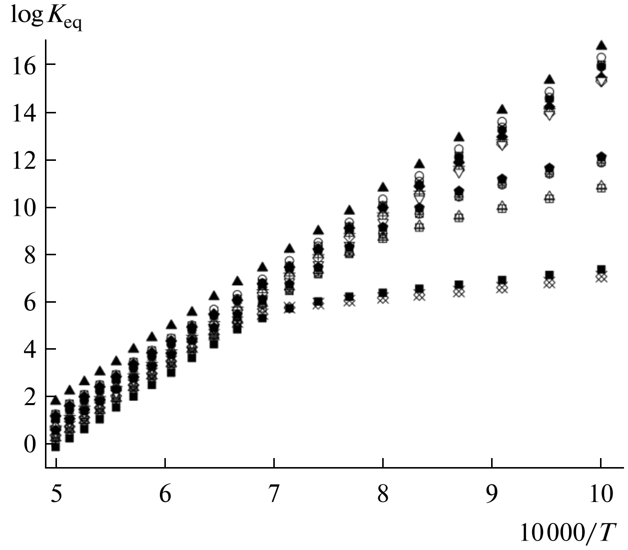

Fig. 5. Temperature dependence of the reaction equilibrium constant for formation of K_2SO_4 in the gaseous phase of combustion products of coals under consideration according to the thermodynamic calculations at the first stage.

$$\left.\begin{aligned} N_{\mathrm{KOH}}^2 / N_{\mathrm{K_2SO_4}} &= K_{\mathrm{eq}} \\ 2N_{\mathrm{KOH}} + N_{\mathrm{K_2SO_4}} &= \Sigma_{\mathrm{K}} \end{aligned}\right\}. \tag{3}$$

The solution of set (3) has the following form:

$$\begin{gathered} N_{\mathrm{K_2SO_4}} = \left(\sqrt{1 + 8\Sigma_{\mathrm{K}} K_{\mathrm{eq}}} - 1\right)^2 \Big/ 16K_{\mathrm{eq}} \\ \Sigma_{\mathrm{K}} = N_{\mathrm{K}}^0 - \Delta N_{\mathrm{K}}. \end{gathered} \tag{4}$$

Here, N_{K}^0 is the potassium concentration in coal; ΔN_{K} is the loss of potassium in the gaseous phase, which was determined at each step of numerical integration via Ω_3 (see below); and K_{eq} is the equilibrium constant for the reaction of potassium sulfate formation in the gaseous phase of combustion products. Based on the data calculated at the first stage (see Fig. 5), the temperature dependences of the equilibrium constants for all coals under consideration were approximated by a two-term polynomial as follows:

$$\log K_{\mathrm{eq}}^{(i)} = A_i + B_i / T. \tag{5}$$

The coefficients of the polynomial for the studied coals are listed in Table 2. The difference between the curves plotted for different coals is related to the fact that set of equations (3) does not take into account the different contents of sulfur and ash-forming elements in specific coals.

In accordance with the common approach, the kinetic equation describing the droplet size distribution function and its numerical solution by the moments method were used to simulate the process of the bulk condensation of supersaturated vapor. In the case of homogeneous condensation with no allowance for the droplet coagulation, this equation has the following form (see, e.g., [17]):

$$v\frac{\partial f}{\partial x} + \frac{\partial(\dot{r}f)}{\partial r} = \frac{I}{\rho_\Sigma}\delta(r - r_{\mathrm{cr}}), \tag{6}$$

where f is the particle mass size distribution function normalized with respect to the number of droplets in unit mass of the vapor–gas–droplet mixture, v is the flow velocity, x is the coordinate along the flow axis, r is the droplet radius, $\dot{r}$ is the rate of particle growth, I is the rate of nucleation, ρ_Σ is the density of the vapor–gas–droplet mixture, δ is the Dirac delta-function, and r_{cr} is the critical droplet radius. Provided that the droplet size is much smaller than the mean free path, Eq. (6) is successfully solved by the moments method, which yields a set of moment equations that is equivalent to Eq. (6) for the first four moments of the distribution function [17]:

$$\frac{d\Omega_n}{dx} = n\frac{\dot{r}}{v}\Omega_{n-1} + \frac{I}{v\rho_\Sigma} r_{\mathrm{cr}}^n. \tag{7}$$

The distribution function moments are determined in the following way:

$$\Omega_n = \int_{r_{\mathrm{cr}}}^{\infty} r^n f dr. \tag{8}$$

The parameters of a condensation aerosol are expressed via distribution function moments as follows:

the number of droplets in unit volume is

$$n_{\mathrm{d}} = \rho_\Sigma \Omega_0,\ \mathrm{m}^{-3}, \tag{9}$$

Table 2. Coefficients of polynomial (5) used to approximate the temperature dependence of reaction equilibrium constant for K_2SO_4 formation in gaseous phase

No.	Coal	A_i	$B_i/10^4$	A_{i1}	$B_{i1}/10^4$	T_1, K
1	Krasnoyarskugol', Beresovskii opencast, RF	−15.0893	2.9927	2.4752	0.4909	1424.3
2	Kyznetsk basin, CC2CCPOKI, RF	−14.4774	2.9604	2.1216	0.9737	1196.9
3	Kyznetsk basin, Mokhovskoi opencast, RF	−14.5768	2.9692	1.1322	0.9679	1274.0
4	Kyznetsk basin, Mokhovskoi opencast, RF	−14.5247	2.9610	1.2465	0.9648	1265.7
5	Pechora basin, Vorkutinskaya mine, RF	−14.0255	2.9372	2.4241	0.9678	1197.2
6	Moscow Region Basin, Novomoskovskaya mine, RF	−13.6649	2.9651	–	–	–
7	Khabarovsk Territory, Urgal'skoe deposit, RF	−14.3520	2.9481	2.9162	0.4099	1469.8
8	Chukotka, Bukhta Ugol'naya deposit, RF	−13.4450	2.8886	–	–	–
9	Republic of Sakha, Neryunginskoe deposit, RF	−14.6787	2.9658	2.1570	0.9742	1183.0
10	Donetsk basin, A, shtyb, SSh, Ukraine	−12.8099	2.8692	–	–	–
11	Ekibastuz basin, Kazakhstan	−12.8082	2.8379	–	–	–
12	Yanzhou, Cina	−12.8733	2.9527	–	–	–
13	YZLS, Cina	−13.4484	2.9636	–	–	–
14	Baotou, Cina	−13.4267	2.9232	–	–	–
15	Wangfg, Cina	−13.8906	2.9051	–	–	–

the average droplet size (radius) is

$$r_d = \Omega_1/\Omega_0, \text{ m}, \tag{10}$$

and the mass concentration of droplets is

$$\rho_l = 4\pi\rho_l\rho_\Sigma\Omega_3/3, \text{ kg/m}^3. \tag{11}$$

The distribution function itself is restored from the results of the solution. Set of equations (7) was integrated using the classical Volmer–Frenkel–Zel'dovich theory [18] to calculate the rate of nucleation and the Hertz–Knudsen formula [19] to calculate the rate of droplet growth.

The results of calculating the process of condensation aerosol formation are illustrated in Figs. 6–10. According to the data in Fig. 6, allowance for the condensation process kinetics makes it possible to describe the passage from the frozen (with respect to condensation) to the equilibrium state as applied to potassium sulfate concentration in the gaseous phase. As follows from Figs. 7 and 8, as the potassium content (N_K^0) in a coil diminishes, the number of formed submicron particles increases, while their sizes decrease. This seems to be associated with a reduction in growth rate of particles being formed with a decrease in the N_K^0 value, which results in a slower elimination of supersaturation upon the cooling of combustion products. In accordance with the data presented in Figs. 9 and 10, the particle size distribution corresponds to the lognormal law. The variance of the distribution decreases with a rise in N_K^0. The use of condensation coefficient $\alpha = 0.1$ when calculating the growth rate of particles ensures agreement with experimental data [5] with respect to average particle size $d_p = 0.06$ μm for Chinese coals.

CONCLUSIONS

1. The results of the thermodynamic analysis of the composition of combustion products of coals with

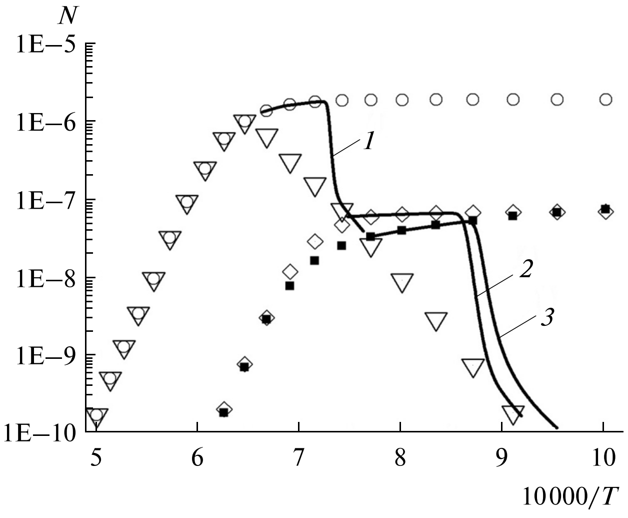

Fig. 6. Temperature dependence of the amount of K_2SO_4 (moles) in the gaseous phase of combustion products during the bulk condensation (solid lines) for three types of coals from (*1*) Donetsk, (*2*) Kuznetsk, and (*3*) Berezovskaya deposits. Triangles denote the curve for the two-phase thermodynamic equilibrium of potassium sulfate. Circles, squares, and rhombs denote the curves for the one-phase equilibrium (frozen condensation).

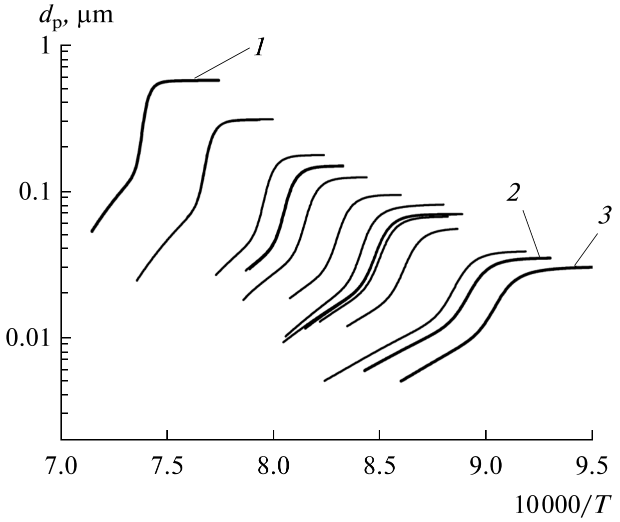

Fig. 7. Variations in the average particle size during bulk condensation in combustion products of all considered coals, including those from (*1*) Donetsk ($N_\mathrm{K}^0 = 0.36\text{E-}5$), (*2*) Kuznetsk ($N_\mathrm{K}^0 = 0.134\text{E-}6$), and (*3*) Berezovskaya ($N_\mathrm{K}^0 = 0.198\text{E-}6$) deposits.

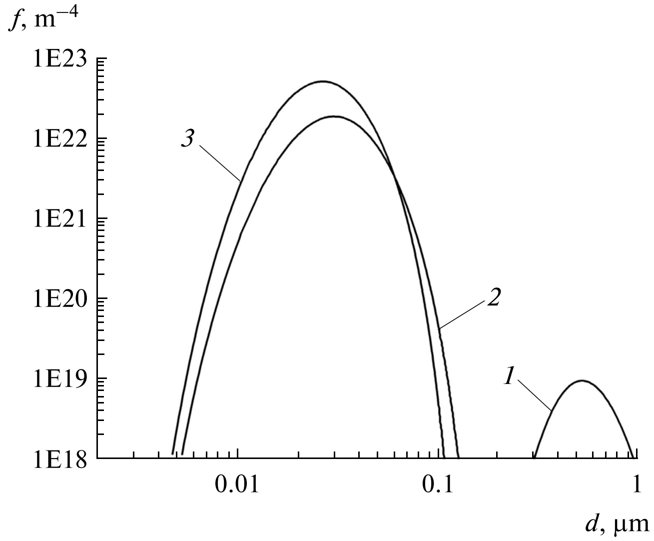

Fig. 9. Size distribution functions for particles resulting from the bulk condensation in combustion products of coals from (*1*) Donetsk, (*2*) Kuznetsk, and (*3*) Berezovskaya deposits. Normalization has been carried out with respect to the number concentration of droplets.

(variant 1) and without (variant 2) allowance for potassium and sodium aluminosilicates have shown that, according to variant 2, potassium and sodium compounds may exist in the gaseous phase at temperatures lower than the combustion temperatures that are realized in the most widely used furnaces.

2. Based on the results obtained, a closed model has been proposed for the formation of submicron particles in coal combustion products in the case of variant 2 (with no regard to the formation of aluminosilicates), this model yielding the upper estimate for the content of submicron particles in combustion products.

3. Using computer-assisted realization of the proposed model, the numerical simulation has been performed for the bulk condensation of potassium sulfate vapor in a flow of combustion products upon their cooling in a technological path. Data on the number

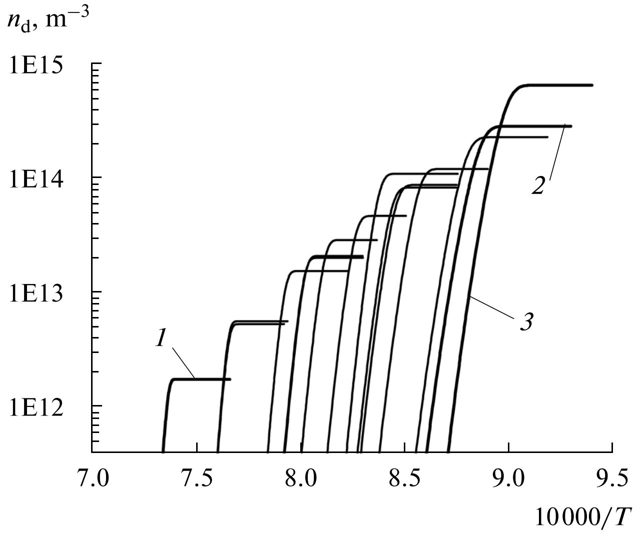

Fig. 8. Variations in the number concentration of particles during bulk condensation in combustion products of all considered coals, including those from (*1*) Donetsk, (*2*) Kuznetsk, and (*3*) Berezovskaya deposits.

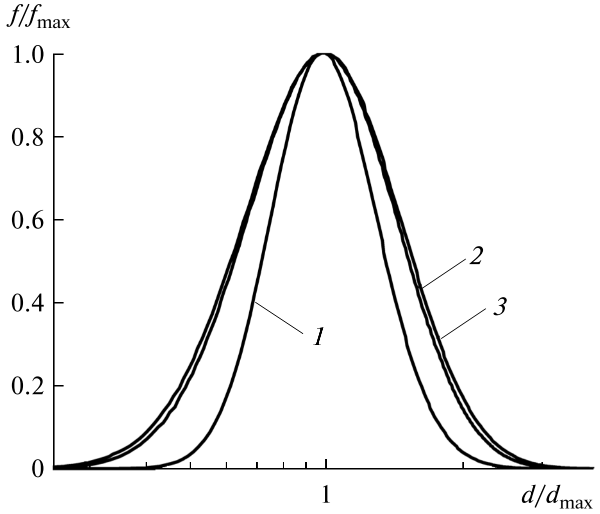

Fig. 10. Size distribution functions for particles resulting from bulk condensation in combustion products of coals from (*1*) Donetsk, (*2*) Kuznetsk, and (*3*) Berezovskaya deposits. Normalization has been carried out with respect to parameters corresponding to the $f(d)$ function maximum.

concentration and size distribution of particles being formed have been obtained. Agreement with experimental data on the average particle size has been achieved at a reasonable value of the free parameter of the model.

4. The role of other ash-forming elements (in addition to potassium) in the formation of submicron particles in coal combustion products is to be considered later.

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REFERENCES

1. Dockery, D.W., Pope, C.A., Xu, X.P., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G., and Speizer, F.E., *New Engl. J. Med.*, 1993, vol. 329, p. 1753.
2. Vejahati, F., Xu, Z., and Gupta, R., *Fuel,* 2010, vol. 89, p. 904.
3. Soco, E. and Kalembkiewicz, J., *Fuel*, 2009, vol. 88, p. 1513.
4. Li, J., Zhuang, X., and Querol, X., *Fuel*, 2011, vol. 90, p. 240.
5. Zhang, L. and Ninomiya, Y., *Fuel*, 2006, vol. 85, p. 194.
6. Lockwood, F.C. and Yousif, S., *Fuel Process. Technol.*, 2000, vol. 65.
7. Tomeczek, J. and Palugniok, H., *Fuel*, 2002, vol. 81, p. 1251.
8. Kortsenshtein, N.M. and Samuilov, E.V., *Izv. Ross. Akad. Nauk, Energ.*, 2005, no. 3, p. 169.
9. Vdovchenko, V.S., Martynova, M.I., Novitskii, M.V., and Yushina, G.D., *Energeticheskoe toplivo SSSR: spravochnik* (USSR Energy Fuel: A Handbook), Moscow: Energoizdat, 1991.
10. Gerasimov, G.Ya., Zhegul'skaya, N.A., Rozhdestvenskii, I.B., Samuilov, E.V., and Sheveleva, N.A., *Mat. Model.*, 1998, no. 10, p. 3.
11. *Termodinamicheskie svoistva individual'nykh veshchestv* (Thermodynamic Properties of Individual Substances), Glushko, V.P., Gurvich, L.V., Bergman, G.A., Veits, I.V., Medvedev, V.A., Khachkuruzov, G.A. and Yungman, V.S., Eds., vols. 1–4, Moscow: Nauka, 1978.
12. *JANAF Thermochemical Tables,* nos. 135–137.
13. *JANAF Thermochemical Tables. Supplement, J. Phys. Chem. Ref. Data*, 1982, vol. 11, p. 695.
14. Shpirt, M.Ya., Kler, V.R., and Pertsikov, I.Z., *Neorganicheskie komponenty tverdykh topliv* (Inorganic Components of Solid Fuels), Moscow: Khimiya, 1990.
15. Lebedeva, L.N, Kortsenshtein, N.M., and Samuilov, E.V., *Thermal Engineering*, 2014, vol. 61, no. 12, p. 911.
16. Lebedeva, L.N, Kortsenshtein, N.M., and Samuilov, E.V., *Khim. Tverd. Topl.,* 2012, no. 4, p. 28.
17. Sternin, L.E., *Osnovy gazodinamiki dvukhfaznykh techenii v soplakh* (Fundamentals of Gas Dynamics of Two-Phase Flows in Nozzles), Moscow: Mashinostroenie, 1974.
18. Kashchiev, D., *Nucleation. Basic Theory with Applications*, Oxford: Butterworth-Heinemann, 2000.
19. Fuchs, N.A., *Evaporation and Droplet Growth in Gaseous Media*, Pergamon Press, New York, 1959.

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