Numerical simulation of submicron particles formation by condensation at coals burning

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Abstract. The thermodynamic analysis of the composition of the combustion products of 15 types of coals was carried out with consideration for the formation of potassium and sodium aluminosilicates and solid and liquid slag removal. Based on the results of the analysis, the approximating temperature dependences of the concentrations of condensed components (potassium and sodium sulfates) were obtained for the cases of two-phase and single-phase equilibriums; conclusions on the comparative influence of solid and liquid slag removal on the probability of the formation of submicron particles on the combustion of coals were made. The found dependences was make it possible to perform a numerical simulation of the bulk condensation of potassium and sodium sulfate vapors upon the cooling of coal combustion products in a process flow. The number concentration and size distribution of the formed particles have been determined. Agreement with experimental data on the fraction composition of particles has been reached at a reasonable value of a free parameter of the model.

1. Introduction
The emission of submicron particles upon the combustion of coals is a source of atmospheric pollution. The current limitations on the concentration of submicron particles in atmospheric air are related to the environmental hazards of these particles [1]. In particular, the US National Ambient Air Quality Standards (NAAQS) specify limitations imposed on the concentration of PM₂.₅ particles, that is, particles smaller than 2.5 μm, in air. Since 2015, the concentration of suspended PM₂.₅ particles in ambient air should also be controlled in the Russian Federation (decree no. 1316-r of the Government of the Russian Federation of July 8, 2015). An additional negative factor related to the formation of particles upon the combustion of coals is that some toxic trace elements contained in coals can be condensed on their surfaces [2–4]. The bulk condensation of the vapors of substances formed from the mineral matter of coals in the course of combustion is considered as a probable mechanism of the formation of submicron particles (solid–vapor–particulate pathway [5–7]).

Information on the parameters of condensation aerosols, which are formed upon the combustion of coals, is necessary for decreasing the emission of submicron particles into the atmosphere due to their trapping. The numerical simulation of a process of bulk condensation can provide this information (the concentration of particles and the particle size distribution). As applied to coal combustion products,
which are multicomponent reacting systems, the use of a complex thermodynamic and kinetic approach is reasonable [8]. At the first stage, the compositions of gas and condensed phases and the condensation order of different substances are determined by chemical thermodynamics methods as the temperature of combustion products decreases along the process flow. The unknown parameters of a condensation aerosol are determined at the second stage from the solution of the kinetic equation of volume condensation taking into account the results of the thermodynamic analysis. In this case, the retention of thermodynamic equilibrium in a gas phase is assumed.

Kortsenshtein et al. [8] reported the results of the implementation of a complex approach to the determination of the parameters of potassium sulfate condensation aerosols in the products of coal combustion, which were also studied in this work. We hypothesized that potassium and sodium aluminosilicates were not formed because the results of the thermodynamic analysis of these coals [9] showed that, with consideration for aluminosilicates, the compounds of potassium and sodium can occur in noticeable amounts in a gas phase only at temperatures higher than the furnace temperature; therefore, their bulk condensation from the combustion products was impossible. At the same time, published experimental data [5] for a portion of coals previously studied by Kortsenshtein et al. [8] showed the particle-size distribution in the coal combustion products is bimodal: a fraction with a diameter of 0.06 μm (of condensation origins) consisted of alkali metal sulfates, and a fraction with a diameter of 1 μm (noncondensation origin) consisted of aluminosilicates. Thus, a model more realistic than that used by Kortsenshtein et al. [8] should take into account the formation of aluminosilicates.

2. Thermodynamic analysis

As previously [8], the combustion products of 15 types of power-generating coals from different deposits in Russia, Ukraine, Kazakhstan and China (PRC) were used as test materials. Note that the compositions of coals varied over wide ranges: the ash content varied from 5.75 to 48%, the sulfur content varied from 0.3 to 6.5%, the potassium content varied from 0.4 to 3.5%, and the sodium content varied from 0.2 to 1.9%. The substances that evaporated at furnace temperatures on the combustion of coal were of interest for studying the mechanism of the formation of highly dispersed fly ash. On the subsequent cooling in the process flow, the submicron particles of fly ash can be formed from them as a result of bulk condensation. Potassium and sodium belong to the most volatile ash-forming elements of coal; therefore, they were chosen for the thermodynamic analysis of the formation and condensation of the compounds of these elements on the combustion of coals. The compositions of coal combustion products depending on temperature were calculated using the modernized computer program TETRAN-PRO (ROSPATENT Reg. No 2016663354) based on a method for the computation of the compositions and properties of multiphase reacting systems [9]. In the calculations, 194 substances formed from 14 atoms were taken into account.

The main idea of the new model consisted in the consideration of the fact that slag removal in coal combustion technology at thermal power plants leads to the removal of the compounds of potassium and sodium. The conversion algorithm is based on the calculation of the total concentration of the elements in the form of compounds with Al and Si in the condensed phase at the temperature of slag removal. The results of this conversion are a decrease in the values of material constants for potassium by a value from 99% to 62% and sodium from 98% to 46% for solid and liquid slag removal. The characteristic temperatures of 1700 and 1900 K were chosen for the solid and liquid slag removal, respectively.

Figures 1 and 2 show the concentrations of potassium and sodium compounds (sulfates) in the gas phase of the combustion products, which were calculated according to the new model taking into account the formation of aluminosilicates and slag removal (the results calculated for all of the coals examined in this work were analogous). For comparison, Figs. 1 and 2 also show analogous data published by Lebedeva et al. [9], who did not consider slag removal. It is evident that the results obtained by Lebedeva et al. [9] gave maximum (if the formation of aluminosilicates was not
considered) or minimum (if it was considered) values of the concentrations of condensed components in the gas phase. The slag removal considered in this work facilitated an increase in the concentration of potassium and sodium sulfates in the gas phase by four to five orders of magnitude, as compared with the data obtained with consideration for aluminosilicates but without slag removal. Note that an increase in the concentration with solid slag removal was greater than that with liquid slag removal. Nevertheless, the increased concentrations remained lower by one or two orders of magnitude than the values obtained without slag removal. Consequently, published data [8], which were obtained without consideration for the formation of aluminosilicates, can be considered as an upper estimate of the concentration of condensation aerosols in the products of coal combustion.

![Figure 1](image1.png)

Figure 1. Numbers of moles of the components containing potassium in the combustion products of coal [8]: (1) without consideration for the formation of aluminosilicates, (2) with consideration for liquid slag removal and the formation of aluminosilicates, (3) with consideration for solid slag removal and the formation of aluminosilicates, and (4) without slag removal with consideration for the formation of aluminosilicates.

Calculated transition temperatures of gaseous potassium and sodium compounds ($K_2SO_4$ and $Na_2SO_4$) into a condensed phase with consideration for slag removal are from 1050 to 1300K; it is evident that the transition temperatures are noticeably lower than the temperature of combustion. Consequently, the bulk condensation of the compounds of potassium and sodium is possible. Besides, the transition temperature for potassium sulfate is higher than that for sodium sulfate; therefore, it can be assumed that the formation of condensation nuclei from potassium sulfate with the subsequent condensation of sodium sulfate on them will occur on the cooling of the combustion products.

3. Kinetic analysis

The driving force of the process of condensation is an increase in the partial pressure of a condensed component relative to an equilibrium value at a specified temperature, which is characterized by the degree of supersaturation. As applied to the case under consideration, the supersaturation ratio can be written in the form

$$s = N'_{K_2SO_4} \left( \frac{N_{K_2SO_4}}{N'_{K_2SO_4}} \right)^{-1}$$

Here, $N_{K_2SO_4}$ is the current number of moles of potassium sulfate in a gas phase, which corresponds to single-phase (with frozen condensation) thermodynamic equilibrium in the gas phase (an analog of partial vapor pressure), and $N'_{K_2SO_4}$ is the number of moles of potassium sulfate in the gas phase, which corresponds to two-phase thermodynamic equilibrium in the system (an analog of saturated
vapor pressure). Note that expressions (1)–(5) written for potassium sulfate (see below) are also valid for sodium sulfate.

Figure 3 shows the temperature dependence of the number of moles of K$_2$SO$_4$ in the gas phase of the coal combustion products. Note that the above dependence has a form characteristic of saturated vapor pressure for all of the coals in the region of two-phase equilibrium. The results calculated for Na$_2$SO$_4$ were analogous. Based on the above data, we obtained temperature approximations for the denominator of expression (1) in the form

$$\log N^o = A + BT$$

(2)

The following set of two equations (the law of mass action and material balance) for the main potassium-containing components (KOH and K$_2$SO$_4$) in the gas phase without condensation in the temperature range of interest was written for determining the numerator of expression (1)

$$N_{K_2SO_4} N_{KOH}^2 = K_{eq}$$

(3)

$$2N_{K_2SO_4} + N_{KOH} = \Sigma_K$$

The solution of set of equations (3) takes the form

$$N_{K_2SO_4} = \left[\left(1 + 8\Sigma_K\right)^{1/2} - 1\right]^2 16K_{eq}^{-1},$$

(4)

$$\Sigma_K = N_K^0 - \Delta N_K.$$
\[ \lg K_{eq}^{(i)} = A_i - B_i T^{-1} \] (5)

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

\[ u \frac{\partial f}{\partial x} + \frac{\partial (kf)}{\partial r} = \frac{I}{\rho \_} \delta(r - r_c) \] (6)

and its numerical solution by the moment’s method [8] were used to simulate the process of the bulk condensation of supersaturated vapor.

Here, \( f \) is the particle mass size distribution function normalized with respect to the number of droplets in unit mass of the vapor–gas–droplet mixture, \( u \) is the flow velocity, \( x \) is the coordinate along the flow axis, \( r \) is the droplet radius, \( \delta \) is the rate of particle growth (Hertz–Knudsen formula [10]), \( I \) is the rate of nucleation (classical Frenkel–Zel’dovich theory [11]), \( \rho \_ \) is the density of the vapor–gas–droplet mixture, \( \delta \) is the Dirac delta function, \( r_c \) is the critical droplet radius.

The results of calculating the process of condensation aerosol formation are illustrated in figures 5–8. As follows from figures 5 and 6, as the potassium content \( N_{K}^{0} \) in a coil diminishes, the number of formed submicron particles increases, while their sizes decrease.

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

**Figure 6.** 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.

A comparison of the calculated and experimental data on the fractional composition of the particles formed during the combustion of two coals of China (PRC) is shown in figures 7, 8. Agreement with experimental data has been reached at a reasonable value of a free parameter of the model.
4. Conclusions

1. According to the obtained data, the depletion of potassium and sodium in the combustion products at solid slag removal was higher than at liquid slag removal. Consequently, the probability of the formation of dangerous aerosols is lower.

2. Comparison of the results of calculations and experiments confirms the reliability of the proposed model.

3. The task of further research is to take into account the compounds of potassium and sodium not only with sulfur, but also with phosphorus.

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